

Environmental Security Technology Certification Program

(ESTCP)

Final Report

CU-0312

Perchlorate Removal, Destruction, and Field Monitoring Demonstration

Applied Research Associates, Inc.

Panama City, FL



**Environmental Security
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a. NAME (Last, First, Middle Initial) Rusk, Jennifer	b. TELEPHONE NO. (Include Area Code) 703-326-7801
---	--

5. PRIOR COORDINATION

a. NAME (Last, First, Middle Initial) Smith, Bradley Leeson, Andrea	b. OFFICE/AGENCY ESTCP Deputy Director ESTCP Program Manager	c. TELEPHONE NO. (Include Area Code) 703-696-2121 703-696-2118
---	--	--

6. REMARKS

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Table of Contents

List of Figures	iv
List of Tables	v
Acronyms	vi
1. Introduction	1
1.1 Background	1
1.2 Objectives of the Demonstration	1
1.3 Regulatory Drivers	2
1.4 Stakeholder/End-User Issues	2
2. Technology Description	3
2.1 Technology Development and Application	3
2.2 Previous Testing of the Technology	9
2.3 Factors Affecting Cost and Performance	9
2.4 Advantages and Limitations of the Technology	9
3. Demonstration Design	11
3.1 Performance Objectives	11
3.1.A. Ion Exchange	11
3.1.A.1. System Operability	11
3.1.A.2. Regulatory Standard	12
3.1.A.3. Low Treatment Cost	12
3.1.A.4. Regeneration without Loss of Capacity	12
3.1.A.5. Regeneration Efficiency	13
3.1.A.6. Treating Spent Regenerant	14
3.1.A.7. Capacity – Bed Volumes Treated	15
3.1.A.8. Treatment flowrate	16
3.1.B.1. Near real-time perchlorate field monitoring capability	16
3.1.B.2. Measurement accuracy	16
3.1.B.3. Detection limit	16
3.2 Selecting Test Site(s)	16

3.3 Test Site Description	17
3.4 Pre-Demonstration Testing and Analysis	19
3.5 Testing and Evaluation Plan	19
3.5.1 Demonstration Installation and Start-Up.....	19
3.5.2 Period of Operation	21
3.5.3 Amount /Treatment Rate of Material to be Treated.....	22
3.5.4. Residuals Handling	22
3.5.5 Operating Parameters for the Technology	22
3.5.6 Experimental Design.....	23
3.5.7 Sampling Plan	27
3.5.8 Demobilization	29
3.6 Selection of Analytical/Testing Methods	30
3.7 Selection of Analytical/Testing Laboratory.....	30
4. Performance Assessment.....	31
4.1 Performance Criteria.....	31
4.2 Performance Confirmation Methods	32
4.3 Data Analysis, Interpretation and Evaluation.....	34
5. Cost Assessment.....	36
5.1 Cost Reporting.....	36
5.1.1 Capital Cost.....	36
5.1.1.1 Application Scenarios	36
5.1.1.2 Basis	36
5.1.1.3 Major Equipment.....	37
5.1.2 Operating and Maintenance Cost	37
5.1.2.1 Primary O&M Cost Components.....	37
5.1.2.2 O&M Cost Basis	38
5.1.3 Economy of Scale.....	41
5.2 Cost Analysis.....	41
5.2.1 Major Cost Drivers.....	41

5.2.1.1 Groundwater Alkalinity.....	41
5.2.1.2 Perchlorate Concentration.....	42
5.2.1.3 Treated Water Alkalinity.....	42
5.2.1.4 Resin Regeneration Cost.....	42
5.2.1.5 WBA Resin Cost.....	43
5.3 Cost Comparison.....	43
6. Implementation Issues.....	46
6.1 Environmental Checklist.....	46
6.2 Other Regulatory Issues.....	46
6.3 End-User Issues.....	46
6.4 Lessons Learned.....	47
6.4.1 Perchlorate Monitor.....	47
6.4.2 Operation and Regeneration of the WBA Resin Treatment System.....	47
7. References.....	50
8. Points of Contact.....	51
Appendix A. Summary of Experiments and Results	
Appendix B. Quality Assurance Program Plan	
Appendix C. Health and Safety Plan	
Appendix D. Tests using Rohm and Haas Resin – PWA2	

List of Figures

Figure 2-1. Demonstration Process.....	4
Figure 2-2. Pretreatment.....	5
Figure 2-3. Ion Exchange.....	6
Figure 2-4. Field Monitor.....	7
Figure 2-5. Post Treatment.....	8
Figure 3-1. Results from Treating Spent Regenerant using Scavenger Resin.....	14
Figure 3-2. Results from Treating Spent Regenerant using Biodegradation.....	15
Figure 3-3. Wells Available for Demonstration at Redstone Arsenal.....	18
Figure 3-4. Candidate Wells Selected for Demonstration.....	18
Figure 3-5. Well RS498 with Well-Pump and Tank.....	20
Figure 3-6. Final prototype as installed at Huntsville.....	21
Figure 3-7. Duration of each Test Period.....	21
Figure 3-8. Single-Pass Regeneration.....	25
Figure 3-9. Batch Regeneration.....	25
Figure 3-10. Scavenger Apparatus.....	26

List of Tables

Table 2-1. Field Monitor Volume Requirements based on MDL and Linear Range	7
Table 2-2. Design Criteria.....	8
Table 3-1. Performance Objectives.....	11
Table 3-2. Capacity of Columns after Regeneration	13
Table 3-3. Regeneration Efficiency	13
Table 3-4. Bed Volumes Treated for each Test Period.....	15
Table 3-5. Amount of Water Treated.....	22
Table 3-6. Laboratory Experiments	23
Table 3-7. Operating Conditions during each Test Period	24
Table 3-8. Objectives for Regeneration and Residual Treatment Experiments.....	24
Table 3-9. Sampling Locations	27
Table 3-10. Sample Parameters, Volume, Preservative Requirements and Hold Times.....	28
Table 3-11. Sampling Summary for ESTCP Pilot Demonstration	28
Table 3-12. Sampling Summary for Regeneration and Residual Treatments	29
Table 3-13. Analytical Procedures used during the Demonstration	30
Table 4-1. Performance Criteria	31
Table 4-2. Expected Performance and Performance Confirmation Methods	32
Table 4-3. Perchlorate Quality Control.....	34
Table 4-4. Split Samples Analyzed for Perchlorate.....	34
Table 4-5. Average Operating pH of Influent and Column Effluents	35
Table 5-1. Summary of Design and Operating Bases.....	36
Table 5-2. Major Equipment.....	37
Table 5-3. Material Cost Basis.....	39
Table 5-4. Cost Summary	40
Table 5-5. Capital and Operating Costs for a 10,000 gpm Treatment System	41
Table 5-6. Summary of Operating Cost Components.....	43
Table 5-7. Cost Comparison Summary.....	44

Acronyms

A&E – Architecture and Engineering
AF – Acre Feet
AFCEE – Air Force Center of Environmental Excellence
AMCOM – Army Aviation and Missile Command
ARA – Applied Research Associates, Inc.
BV – Bed volumes
DAB – decyltrimethylammonium bromide
DOD – Department of Defense
ESTCP – Environmental Strategic Technology Certification Program
gpm – gallons per minute
HASP – Health and Safety Plan
I&C – Instrumentation and Control
ISEP – Ion Separation
IX – Ion Exchange
MCL – Maximum Concentration Limit
MMR – Military Massachusetts Reserve
NPDES – National Pollutant Discharge Elimination System
O&M – Operation and Maintenance
OSHA – Occupational Safety and Health Administration
P2 – Pollution Prevention
PEO – Program Executive Office
psig – pounds per square inch, gauge
PM – Program Manager
ppb – parts per billion
PPE – Personal Protective Equipment
QA – Quality Assurance
QA/QC – Quality Assurance/Quality Control
QAPP – Quality Assurance Project Plan
RfD – Reference Dose
RSA – Redstone Arsenal
SSC – Site Safety Coordinator
TCE – Trichloroethylene
TCE – Trichloroethylene
TPM – Technical Program Manager
VOC – Volatile Organic Carbon
WBA – Weak Base Anion

1. Introduction

1.1 Background

The Department of Defense (DOD) has used perchlorate (ClO_4^-) as an oxidizer in ordnance items and rocket motors for over half a century. This very water soluble and environmentally persistent compound now contaminates drinking water for tens of millions of people in the United States. In 2002, the US Environmental Protection Agency released a provisional perchlorate Oral Reference Dose (RfD), which translated into a drinking water equivalent level of 1 part per billion (ppb). This drinking water equivalent level was recently increased to 24.5 ppb following the release of a report by the National Academy of Science.

The cost for DOD to achieve compliance with these drinking water limits have been estimated to be in the billions of dollars. The current approach is treatment by either ion exchange or biological processes. The ion exchange approach is favored for groundwater and drinking water applications. Existing ion exchange technologies in use today include regenerable ion exchange processes that use salt as the regenerating agent, such as the Calgon ISEP process and other, more conventional lead-lag processes. The non-selective regenerable systems require frequent regeneration and generate large volumes of salt brine containing high concentrations of nitrate, sulfate and perchlorate. The operation and maintenance (O&M) cost from frequent regenerations is high and complicated further by the generation of a waste stream that is becoming more difficult to dispose. Existing ion exchange technologies also include single-use ion exchange processes that use strong base anion resins that are incinerated after their perchlorate loading capacity is reached. Once loaded with perchlorate the single use resins must be removed from the ion exchange vessels and incinerated resulting in high disposal and replacement costs. The work proposed for this demonstration builds upon past research that has been performed to address these problems with current ion exchange technologies. The end goal is to field a more efficient and economical approach to achieving compliance for perchlorate contamination.

1.2 Objectives of the Demonstration

The objectives of this demonstration were to evaluate and demonstrate a complete perchlorate ion exchange process for groundwater that included a unique, regenerable, perchlorate-selective ion exchange resin; an efficient regeneration technique that greatly minimized waste volume; methods for treating regeneration waste from this process that would reduce cost by enabling discharge or reuse; and to demonstrate a new perchlorate field monitor with ppb detection. In order to validate the performance and economics of the proposed processes compared to current perchlorate treatment processes, the following objectives were proposed:

1. Demonstrate perchlorate removal in groundwater from >50 ppb to ≤ 5 ppb with a regenerable, perchlorate-selective ion exchange process.
2. Demonstrate an efficient regeneration technique of the perchlorate-selective ion exchange resin. Regenerant volume should be $< 0.1\%$ of treated groundwater stream.
3. Demonstrate removal or destruction of perchlorate (≤ 5 ppb) in the regenerant stream enabling discharge or reuse of the regenerant stream.

4. Demonstrate the performance of a perchlorate field monitor capable of on-line, real-time perchlorate analysis with a minimum detection limit of 1 ppb.

To achieve these objectives, a demonstration was conducted at Redstone Arsenal, located in Huntsville, Alabama, using groundwater as the medium. Well RS498, a six inch extraction well, was selected for the demonstration having the following anion concentrations: 1500 to 2000 ppb perchlorate; 4 ppm nitrate; 3 ppm sulfate; and 4 ppm chloride.

1.3 Regulatory Drivers

In 1992, the US Environmental Protection Agency established a “provisional” reference dose for perchlorate of 4 parts per billion. Since that time the “safe” level for perchlorate in drinking water has been a much studied and debated topic. A number of states including California, Arizona, Maryland, Massachusetts, Nevada, New Mexico, New York, and Texas have all established criteria for perchlorate in drinking water. These standards have ranged from 1 ppb to 32 ppb. In 2002, the US EPA released a provisional perchlorate Oral Reference Dose (RfD), which translated into a drinking water equivalent level of 1 ppb. Due to much controversy over the establishment of a drinking water standard, the National Academy of Science was tasked with analyzing the available scientific data and recommending a “safe” standard. Following the much anticipated release of this report by National Academy of Science, the drinking water equivalent level was increased to 24.5 ppb. It is not guaranteed or clear at this time if states that regulate perchlorate will follow EPA’s lead and increase their more stringent standards to reflect the latest scientific recommendations.

1.4 Stakeholder/End-User Issues

During ESTCP project CU-0312, ARA demonstrated an ion exchange process using weak base anion (WBA) resins that are regenerable as well as perchlorate-selective. Some of the issues that end-users and stakeholders face for ion exchange technologies include a simple and effective regeneration process, disposal of concentrated regenerant streams, and cost. The results from this 15-week pilot demonstration indicate that there are advantages of this ion exchange technology that mitigate these issues. These advantages are listed below:

- Complete ion exchange and regeneration processes controlled by pH
- Regeneration uses low-cost and relatively safe caustic solution
- Low volume of regenerant required for complete resin regeneration (50 times less than brine regenerant required for regenerating SBA resins)
- O&M costs: \$50-100 per acre-ft (Details provided in Section 5.0)

2. Technology Description

2.1 Technology Development and Application

Ion exchange using WBA resin is effective for treating perchlorate contamination in any surface, ground, or drinking water application. The WBA resin selected for this demonstration is regenerable as well as perchlorate-selective. The ion exchange process takes advantage of the pH dependent nature of WBA resins. At low pH, functional groups on these resins have a positive charge (i.e. R-NH_3^+) allowing for anion exchange. However, at high pH, the resin functional groups lose a proton and are uncharged (i.e. R-NH_2) allowing for regeneration. The regenerated, “free-base” form of WBA resin does not attract anions from solution.

The primary advantages of ion exchange using WBA resin are the ease and simplicity of regeneration, the small volume of spent regenerating solution produced, the resulting lower O&M cost of regeneration, and the lower cost and ease of disposal of the spent regenerating solution. Following caustic regeneration of the resin and prior to return to service, ionic groups on the WBA resin must be protonated using a dilute acid solution. Regeneration and protonation solutions are discussed in more detail in the residuals treatment paragraphs, later in this section.

The ion exchange process using WBA resins is comprised of three major operations: pretreatment, ion exchange, and post treatment (Figure 2-1). These operations are described below.

pH Pretreatment (Figure 2.2)

In order for the WBA resin to be effective, the groundwater pH must be below the pKa of the resin. It was determined in laboratory studies that the capacity of the WBA resin for perchlorate increased as pH decreased. These studies indicated that the pH of the feed water needed to be in the range of 2.5-5.5 for effective anion exchange. To accomplish this, groundwater was pumped from the well head to a level-controlled storage tank and then metered into the pressurized pH pretreatment system. This system consisted of a pH controller, an acid feed system, and a circulation pump and mixing vessel. The pH control setting of the pretreatment system was set at a value of 4.0. The system was pressurized to keep carbon dioxide in solution as dissolved carbon dioxide and carbonic acid.

The volume of the pressurized pretreatment system was approximately 4.6 liters. At the operation flow rates of 12, 18, and 24 BV/hr feed rate (2 liters per bed volume), the hydraulic residence time was 11.5, 7.7, and 5.8 minutes, respectively. At operational pH (3 to 5), bicarbonate will be converted rapidly to carbonic acid and achieve equilibrium. A backpressure regulator will maintain constant system pressure. This regulator was positioned after the ion exchange columns and column bypass lines, but before flow through the scavenger resin and post treatment stripping and neutralization.

The pH adjusted groundwater was passed through a micron filter to remove solids prior to entering the ion exchange unit. A pulsation dampener minimized pressure and flow fluctuations in the ion exchange system and a flow totalizer monitored total groundwater volume treated.

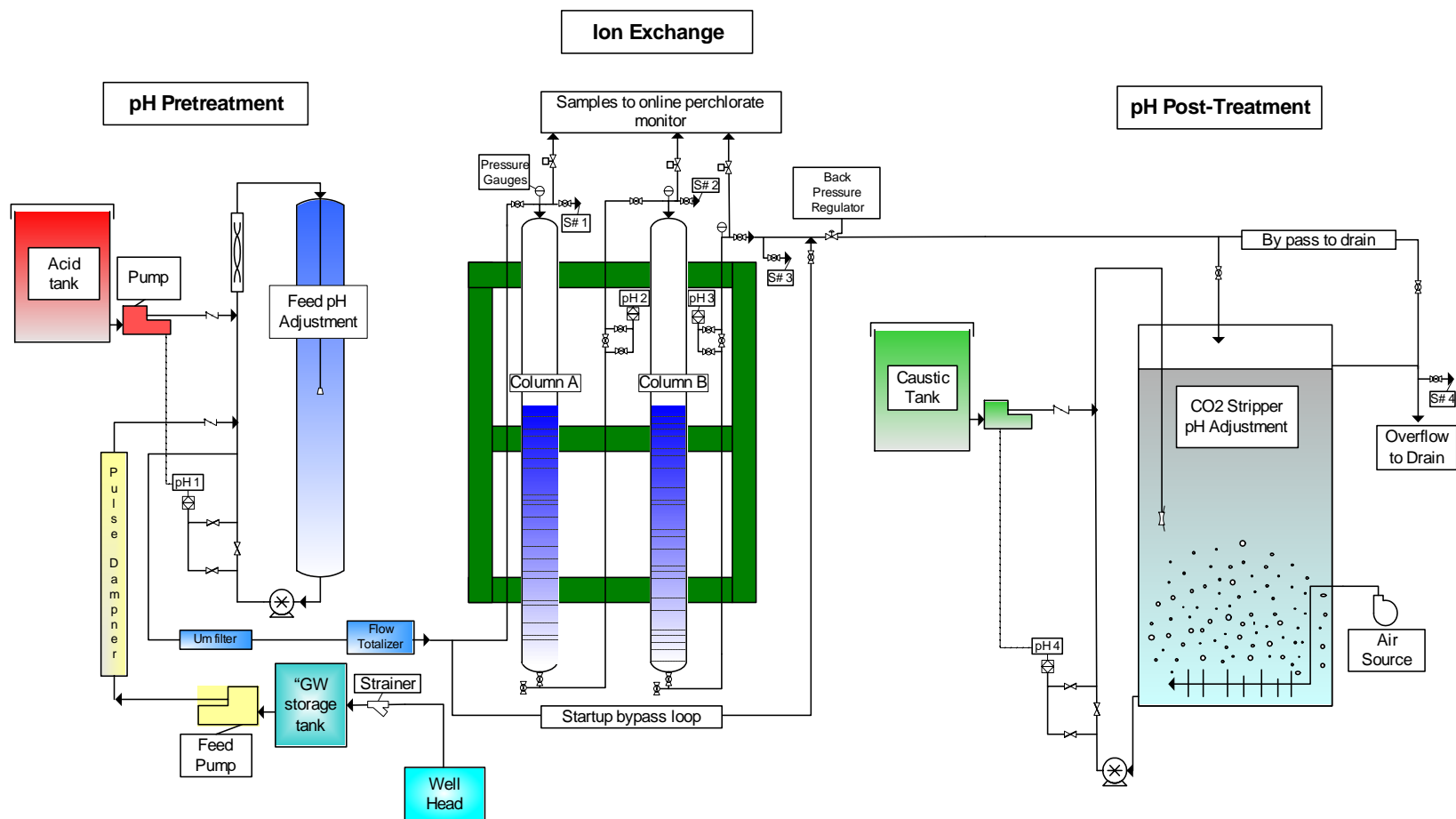


Figure 2-1. Demonstration Process

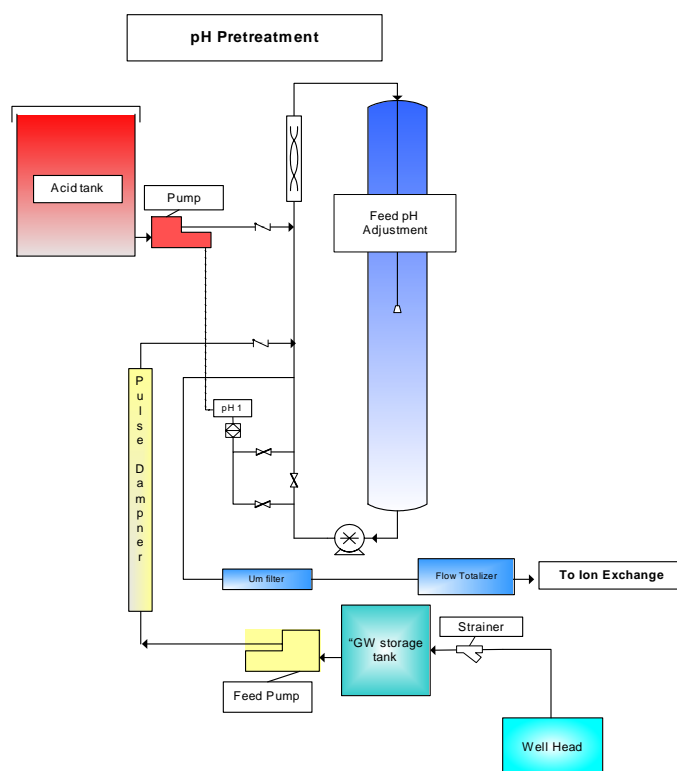


Figure 2-2. Pretreatment

Ion Exchange & Field Monitor

The ion exchange unit, shown in Figure 2-3, consisted of two ion exchange columns in series. The pretreated water passed through these columns in a lead-lag configuration. When perchlorate breakthrough in the lead column exceeded a predetermined value, the column was removed from the system for regeneration, the lag column replaced the lead column, and a freshly regenerated column was installed as the lag column. The removed, perchlorate-loaded column was shipped to ARA's Panama City, Florida laboratory for regeneration and subsequently returned to the field demonstration. This cycle was repeated over five test periods.

Three sample locations, the feed stream and discharge from each column, were configured for both automated and manual sampling. A solenoid valve was configured to control sampling for the perchlorate field monitor. Pressure and pH were also monitored at each sample location. The perchlorate field monitor was configured to control sampling events and data acquisition. At least one time per day, each sample location was to be analyzed for perchlorate by the field monitor. Manual sampling was conducted at least three times per week.

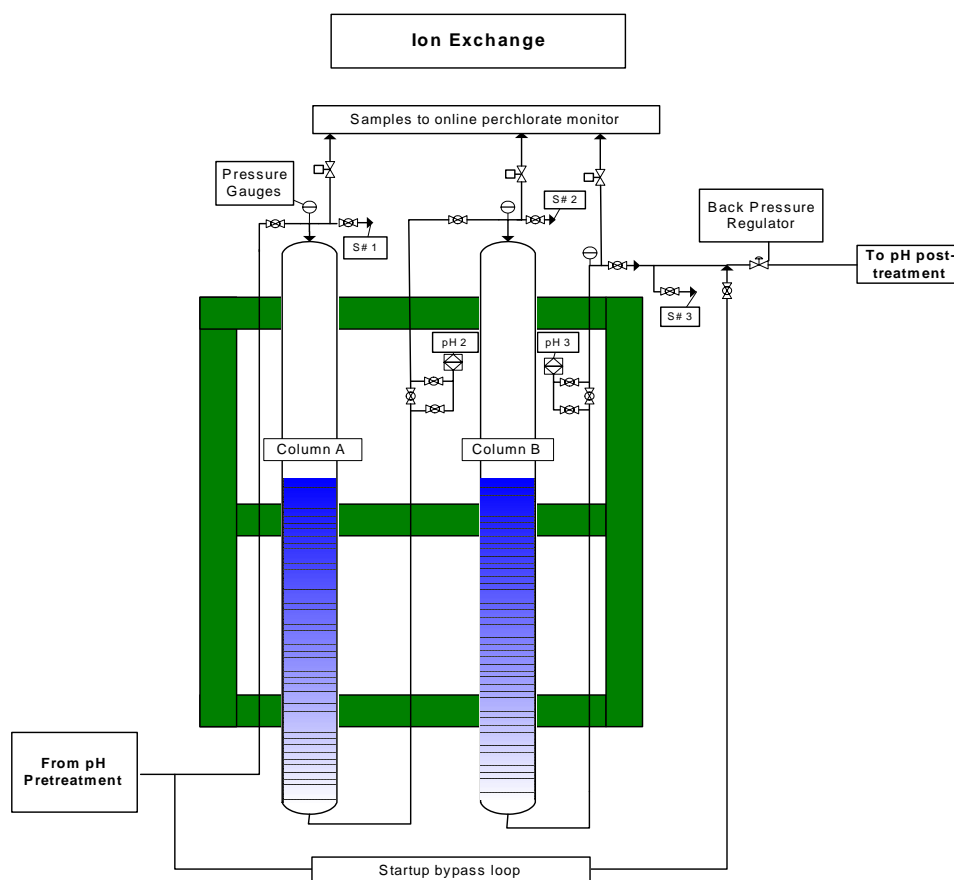


Figure 2-3. Ion Exchange

A schematic depicting operation of the perchlorate field monitor is shown in Figure 2-4. The field monitor chemistry is based on a solid-phase extraction cartridge loaded with styrene-divinylbenzene resin that is preconditioned with decyltrimethylammonium bromide (DAB). DAB is an ion-pairing reagent with a highly specific affinity for perchlorate. The monitor was configured so water samples, daily check standards, and/or deionized water blanks would pass through the cartridge, where perchlorate and small quantities of other major ions are retained. A rinse step would be conducted to remove potential interferences. The perchlorate ion-pair would be eluted from the cartridge with acetone and delivered to a test-tube mounted in a spectrophotometer. Deionized water, a second perchlorate-specific ion-pair, and xylene would then be added. This second ion-pair is brilliant green dye, which competes with the DAB for the perchlorate ion-pair. The exchange of perchlorate from DAB to the brilliant green dye is favored because the dye ion-pairs are strongly hydrophobic and are extracted into the layer of xylene. Following a ten minute equilibration time, the absorbance of dye in the xylene layer would be recorded.

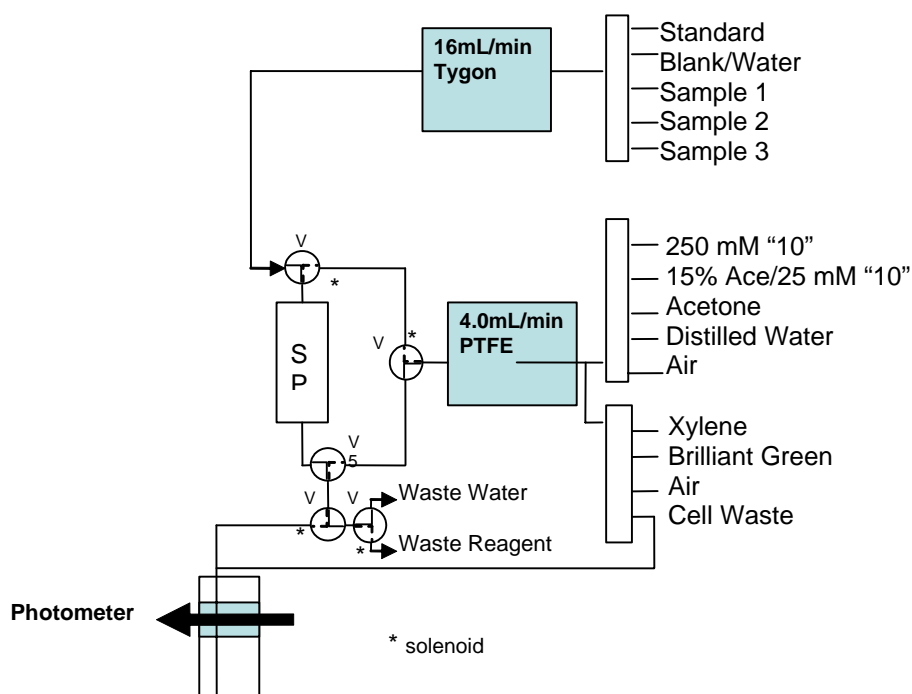


Figure 2-4. Field Monitor

The expected concentration of the sample water determined the volume of samples extracted. Table 2-1 identifies the relationship between sample volumes, linear ranges, and detection limits. The table also identifies the predicted sample volume of each sampling location.

Table 2-1. Field Monitor Volume Requirements based on MDL and Linear Range

Volume (mL)	Detection Limit (ppb)	Linear Range (ppb)	Sample Location
500	1	1-30	Column 2 Effluent
20	25	25-750	Column 1 Effluent
10	50	50-1500	Groundwater

Post Treatment:

Following ion exchange, the treated groundwater underwent post treatment to neutralize the effluent before discharge. Neutralization was accomplished by air stripping carbon dioxide from the effluent and adding of caustic (Figure 2-5). Adequate residence time (>5hours) was provided to assure equilibrium was attained. By controlling pH of the effluent, the degree of CO₂ removal and resulting alkalinity was precisely controlled.

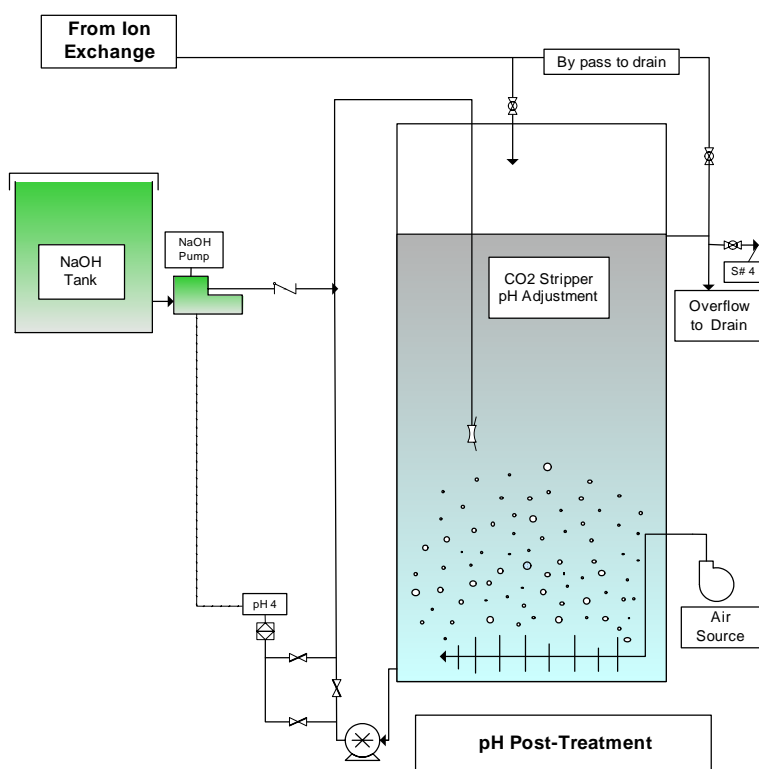


Figure 2-5. Post Treatment

Table 2-2 lists the design criteria for the demonstration.

Table 2-2. Design Criteria

Criteria	Minimum	Maximum	Nominal Design
Column inside diameter (in)	2.049	2.049	2.049
Resin bed depth (in)	32	40	36
Resin volume (liters)	1.73	2.16	1.95
Flow rate (BV/hr)	12	28	16
Flow rate (gal/hr)	6.2	14.4	8.2
Pressure drop (psig)	5.0	12.2	6.8
Operating pressure (psig)	10	30	20
Operating pH	3.0	5.0	4.0
Discharge pH	7.0	8.3	7.6

Residuals Treatment:

Both biodegradation and super-loading tests were conducted on spent regenerant from the field demonstration. In addition, three different regeneration techniques were employed: single-pass, batch, and batch with “zero discharge” regeneration. Anion analyses were conducted on each

bed volume or batch of spent caustic regenerating solution and rinse water to determine regeneration effectiveness. Results of residual studies can be found in Appendix A Section 4.0.

2.2 Previous Testing of the Technology

Prior to this demonstration, application of weak base anion resin ion exchange technology for perchlorate removal had only been conducted in laboratory-scale equipment as part of this project. The field monitor was derived from a similar monitor developed for explosives testing, but had only been tested in the laboratory under manual operation.

2.3 Factors Affecting Cost and Performance

The water quality parameters that affect cost and performance are alkalinity, hardness, perchlorate concentration, sulfate concentration, and treated water alkalinity. The amount of acid required to achieve operating pH is directly proportional to feed water alkalinity and; therefore, pretreatment cost. Perchlorate concentration dictates the resin treatment capacity and regeneration frequency which affects regeneration cost. In addition, perchlorate concentration and regeneration frequency impact the amount of spent regenerating solution and treatment cost. Hardness and desired alkalinity of treated water affect the caustic requirement for neutralization, which affects neutralization cost.

Sulfate concentration can also affect pretreatment cost. The most economical pretreatment approach is to use sulfuric acid. However, the uses of sulfuric acid will increase the residual sulfate concentration. If feed alkalinity and sulfate concentrations are high, residual sulfate concentration could exceed the Secondary Water Treatment guideline of 250 mg/L. In this case, it may be necessary to replace some or all of the sulfuric acid with the more expensive hydrochloric acid.

2.4 Advantages and Limitations of the Technology

Three technologies are currently used commercially for remediating perchlorate contaminated groundwater: 1) biodegradation, 2) ion exchange using regenerable resins, and 3) ion exchange using non-regenerable or disposable resins. The proposed technology takes advantage of the performance, favorable public perception, and regulatory acceptance of ion exchange while minimizing the liabilities of current ion exchange systems. These liabilities include: 1) the high cost of perchlorate-selective resins currently in use, 2) large volume of residuals generated by regenerable systems, 3) the difficulty and high cost of treating residuals, and 4) resin replacement and incineration costs for non-regenerable systems.

Limitations of the WBA technology are associated with the performance parameters discussed in the previous section. The weak base, perchlorate-selective resins currently being evaluated do not have the treatment capacity of strong base, perchlorate-selective resins. Even so, overall cost saving may be substantial since these resins can be economically regenerated. A comparable cost SBA resin (\$600/ft³) must have a treatment capacity 30 times greater in order to achieve the same treatment cost. It is physically impossible for SBA resins to exchange the four equivalents of perchlorate per liter of resin necessary to be cost competitive with WBA resins. The SBA resins typically have approximately two equivalents per liter of total exchange capacity and only

a small fraction of exchanged anions are perchlorate. SBA resins cannot achieve this high selectivity and high capacity. Even if this capacity could be achieved, physical limitation will limit practical treatment capacity. At 3 gpm/ft³, a typical treatment rate for a commercial application of single-use SBA resins, a vessel would have to remain on-line over two years to achieve the necessary performance. Physical plugging, channeling, algae, bacterial growth, compaction, etc., would likely limit the period of performance to far less than two years. Since the WBA resin would be regenerated every four weeks for the above scenario, physical problems would be avoided. The only commercial regenerable SBA system (ISEP) regenerates each resin vessel every day.

Pretreatment and post treatment do add process complexity compared to single-use ion exchange systems. However, the complexity is not significantly greater than the only commercial, regenerable ion exchange perchlorate treatment technology currently in use – ISEP. Pretreatment and post treatment unit operations are very straight-forward pH control processes. The WBA resin approach will likely be simpler and smaller than the ISEP process when the treatment and reuse of residuals is considered.

3. Demonstration Design

3.1 Performance Objectives

The primary means used to assess performance was collecting and analyzing groundwater samples before and after treatment (specifically, pretreated groundwater and column effluents). Analytical results were also used to determine the treatment capacity of the WBA resin at the conditions tested. Operational data was used to determine operating cost of this demonstration such as acid and caustic consumption. Table 3-1 lists the performance objectives for this demonstration and if these objectives were met. Details describing how the technology performed for each performance objective are summarized following Table 3-1.

Table 3-1. Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
A. Ion Exchange			
Qualitative	1. System operability	No or few process upsets	Yes
Quantitative	2. Meet perchlorate regulatory standards for potable water	\leq MCL (5ppb)	Yes
	3. Low treatment cost	$<$ \$100/acre-ft	Yes
	4. Ability to regenerate WBA resin base – change in treatment capacity	Capacity \pm 10%	Yes
	5. Efficiency of regeneration	$<$ 0.1 vol% residual	Yes
	6. Treatment of spent regenerating streams – removal of perchlorate	\leq MCL (5 ppb)	Yes
	7. Demonstrate WBA resin capacity	$>$ 6100 BV	Yes
	8. Treatment flowrate	\geq 1.5 gpm/ft ³	Yes
B. Field Monitor			
Quantitative	1. Near real-time perchlorate field monitoring capability	Analysis and reporting of all influent and effluent streams at least once per day	No
	2. Measurement accuracy	\pm 20% of lab result	No
	3. Detection limit	1 ppb	No

3.1.A. Ion Exchange

3.1.A.1. System Operability

The performance metric for assessing system operability was the ability of the system to operate as designed without process upsets or interrupted flow. As described in Section 2-1, this includes three units of operation: pretreatment, ion exchange, and post treatment.

During the demonstration, there was never a flow interruption due to a unit process upset. However, there was one occasion during the two week startup period that the acid pump used in pretreatment lost prime and thus the ability to reduce the pH of the groundwater. Since the process uses weak base anion resin, pretreatment of the influent to decrease the pH is especially important to prevent a process upset by maintaining the resin in the ionized form. Neutral water would neutralize the functional groups preventing anion exchange. Fortunately, the failed pump was realized and corrected before the ion exchange resin was exposed to a large volume of neutral water, which would have led to a process upset. The pump was replaced and pH of the influent was checked frequently using a web-based data acquisition system.

3.1.A.2. Regulatory Standard

A maximum contaminant limit (MCL) has not been established by EPA. For the purpose of evaluating performance, ARA identified 5 ppb as a performance measure (currently, the CA DHS public health goal is 6 ppb). During the first two test periods, perchlorate concentration in lead column effluents was approximately 10-13 ppb until breakthrough. These columns had been pre-loaded and regenerated before put in service during the demonstration. It was determined that perchlorate was leaking from the columns due to insufficient rinsing following preconditioning. The rinse procedure was modified and column 4 was regenerated using the new procedure. Leakage was not observed during the remaining three test periods. The effluent concentration during test periods three through five remained less than 4 ppb until breakthrough occurred.

3.1.A.3. Low Treatment Cost

The calculated unit operation and maintenance cost for this technology in a remediation application is \$84.70/acre-ft. This meets the performance expectation of less than \$100/acre-ft. The assumptions and basis for this value is described in Section 5.

3.1.A.4. Regeneration without Loss of Capacity

Three columns were used during the demonstration. Comparing the capacity of these columns after regeneration was difficult for the following reasons: 1) perchlorate concentration in the groundwater steadily increased from approximately 1400 µg/L to as much as 2200 µg/L, 2) the volume of groundwater treated and the perchlorate breakthrough concentration was different for each column, and 3) the flow rate was increased from 12 BV/hr to 18 and 24 BV/hr. Each of the factors listed affects the final resin capacity for each test period.

In order to compare resin capacities of columns after regeneration, the following assumptions and calculations were made:

1. The resin capacity was determined at 100 µg/L breakthrough for each test period.
2. Based upon the concentration of perchlorate in the groundwater at 100 µg/L breakthrough, a predicted capacity was determined using an isotherm calculation.
3. A ratio of the predicted capacities at the different groundwater feed concentrations (1400, 2200, and 2000 µg/L) was determined.

4. This ratio was used to normalize the capacities at 100 µg/L breakthrough and different feed water concentrations to a capacity at 100 µg/L breakthrough with a groundwater feed concentration of 1400 µg/L.

These values are shown in Table 3-2. The resin capacities calculated for treating a 1400 µg/L perchlorate groundwater and at 100 µg/L breakthrough are within the 10 percent performance criteria.

Table 3-2. Capacity of Columns after Regeneration

Test Period	1	2	3	4	5
Column I.D.	C1	C2	C4	C1	C2
Capacity (meq/L)	87.4	87.5	80.0	130.1	125.4
Capacity at 100 µg/L BT (meq/L)	72.3	72.9	68.9	102.9	96.9
Feed Water Conc. At 100 µg/L BT (µg/L)	1400	1400	1400	2200	2000
Predicted Capacity at Feed Water Conc (Isotherm) (meq/L)	94.4	94.4	94.4	130.9	121.8
Capacity Ratio	1	1	1	0.72	0.77
Normalized Resin Capacity (meq/L)	72.3	72.9	68.9	74.2	75.1

3.1.A.5. Regeneration Efficiency

The performance metric to determine regeneration efficiency was having a waste volume residual less than 0.1%. The treated water volumes for each test period and the spent regenerant volumes are identified in Table 3-3. For each test period, the waste volume residual is approximately half of the performance goal. The regenerant volumes do not include rinse water as this water would be reused.

A zero discharge procedure was demonstrated on the residual from Test Period 1 using scavenger resin. The scavenger resin removed perchlorate from the spent regenerant waste providing a perchlorate-free effluent that could be discharged to sewer. The zero discharge scavenger resin process and results are described in Sections 3.1.A.6 and Appendix A Section 4.0.

Table 3-3. Regeneration Efficiency

Test Period	1	2	3	4	5
Water Treated (L)	14259	11894	10229	12615	12942
Regenerant (L)	6.08	6.00	6.31	6.35	5.96
% Residual	0.04%	0.05%	0.06%	0.05%	0.05%

3.1.A.6. Treating Spent Regenerant

The performance criteria for treating spent regenerant was to remove perchlorate from the spent regeneration solutions to less than 5 µg/L. Two processes were evaluated for treating spent regenerant including a scavenger process and biodegradation. The results of these treatment processes are shown in Figures 3-1 and 3-2. Details of these processes can be found in Appendix A Section 4.2.2.

The spent regenerant collected from regeneration of column 1 during the first test period was treated using a scavenger process. The spent regenerant was passed over four columns, arranged in series, containing 90cc of strong base anion resin (Purolite A600). Perchlorate concentration of effluents from scavenger columns 1 and 2 is shown in Figure 3-1 (analyzed using EPA Method 314.0). The results indicate that perchlorate in the spent regenerant was removed to concentrations below the detection limit (4 µg/L) after passing through the first two columns arranged in series. Perchlorate concentration of effluents from scavenger column 3 was also below the detection limit (not shown). Perchlorate concentration of effluents from scavenger column 4 was also below the detection limit (not shown).

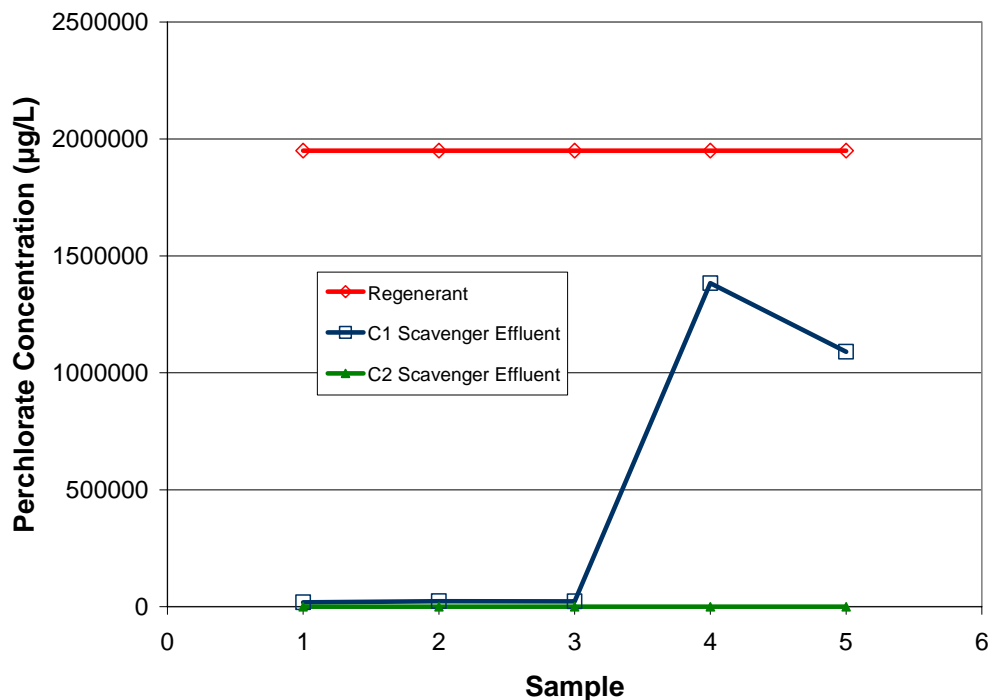


Figure 3-1. Results from Treating Spent Regenerant using Scavenger Resin

Spent regenerant and rinse water from test periods 2 through 5 was biodegraded using two 2.5-liter reactors arranged in series. Perchlorate concentrations of the influent (spent regenerant diluted with the spent rinse water), and effluent from the two reactors (R1 and R2) are shown in Figure 3-2. Ion chromatography analyses were conducted using EPA Method 314.0 and the detection limit was 4 µg/L. Perchlorate concentration in R2 effluent was below the detection limit for most of the experiment. There was a three day period from when

perchlorate concentrations were above the detection limit. This was due to a limitation of nutrient and concentrations returned to below 4 µg/L as soon as the nutrient was increased (See Appendix A Section 4.2.2).

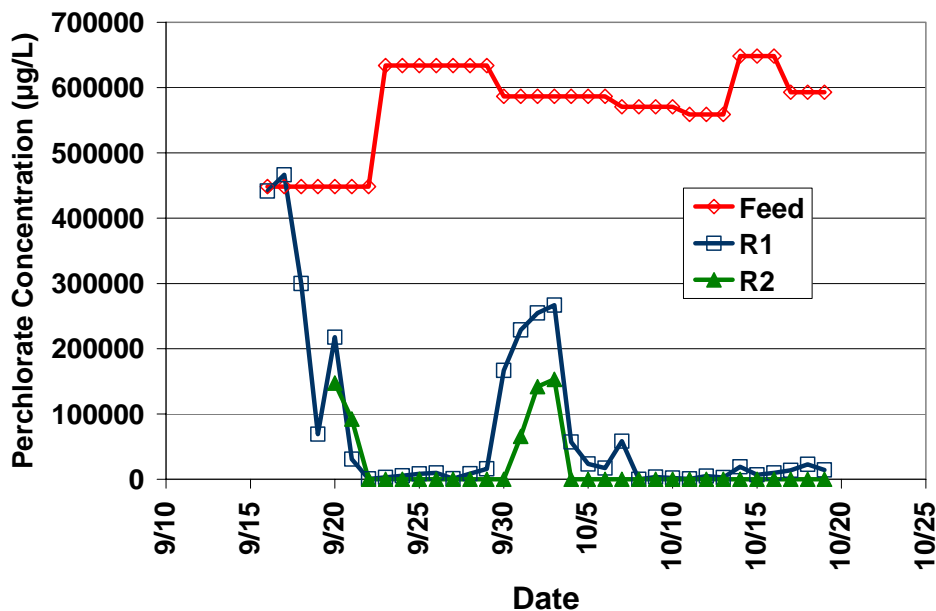


Figure 3-2. Results from Treating Spent Regenerant using Biodegradation

3.1.A.7. Capacity – Bed Volumes Treated

The performance objective for this metric was the ability to treat greater than 6100 bed volumes. This metric was developed based upon having a perchlorate concentration of approximately 1400 µg/L. The volume treated and the perchlorate breakthrough for each test period is listed in Table 3-4. Test periods 1, 4 and 5 exceed the 6100 bed volume metric, even when perchlorate concentration in the groundwater exceeded 2200 µg/L. Test period 2 was only slightly above the performance metric, however, this test period was stopped when breakthrough was only 8.2%. Test period 3 was also stopped early (breakthrough only 7.8%) because of weather threats due to Hurricane Katrina. If not for early termination of this test period, the volume treated should have exceeded 6100 bed volumes.

Table 3-4. Bed Volumes Treated for each Test Period

Test Period	Bed Volumes Treated	Perchlorate Breakthrough (%)
1	7331	19.5
2	6115	8.2
3	5259	7.8
4	6486	26.2
5	6654	49.5

3.1.A.8. Treatment flowrate

The objective for this test period was to demonstrate a treatment rate of at least 1.5 gpm/ft³. Test periods 1 through 3 were conducted successfully at the minimum treatment rate objective (1.5 gpm/ft³). The treatment rates for test periods 4 and 5 were increased to 2.25 and 3.0 gpm/ft³, respectively. The performance was not adversely impacted at these elevated flow rates. Both test periods met the 6100 bed volume treatment metric (Table 3.4).

3.1.B.1. Near real-time perchlorate field monitoring capability

The field monitor was configured in a fiberglass NEMA enclosure and installed in the test trailer at Redstone Arsenal. Three initial failures (two valves and one pump) occurred as a result of unforeseen software problems. Another failure occurred when the program crashed. During this program failure, the FMI pump was left running and the pump emptied the de-ionized water reservoir. As a result, the pump shaft was damaged.

In the two other cases, program crashes caused method steps to be missed resulting in the pump attempting to force fluid through a “dead-headed” three way valve, which then burst from over-pressure. Therefore, the monitor did not operate long enough to generate useful data. It was returned to ARA-NED for trouble-shooting and tests were conducted on surrogate water representing groundwater and column effluents. Details can be found in the response for IPR Action Item #1 submitted on 1 November 2005.¹

3.1.B.2. Measurement accuracy

Although the colorimetric method developed demonstrated high accuracy compared to Method EPA 314.0 during previous testing, this was not the case during this demonstration. The low pH (4.0) of surrogate samples of groundwater and column effluents interfered with the performance of the field monitor. Data indicated that the monitor could work successfully with a system that does not require pH adjustment to 4.0. (See whitepaper response to IPR Action Item #1 submitted on 1 November 2005).

3.1.B.3. Detection limit

The field analyzer was unable to meet the performance objective of a detection limit of 1 µg/L for the same reason listed above. Previous studies using the colorimetric method demonstrated a detection limit less than 1 µg/L when analyzing well water and bioreactor effluents at neutral pH. (See whitepaper response to IPR Action Item #1 submitted on 1 November 2005.)

3.2 Selecting Test Site(s)

The main criteria for site selection included 1) surface and/or groundwater perchlorate contamination levels that range from a few parts-per-billion to hundreds of ppb, 2) existing extraction wells and infrastructure providing access to the contaminated waters, and 3) site interest in hosting the demonstration. Based upon these criteria, Redstone Arsenal, Massachusetts Military Reserve (MMR), and Hill AFB, Utah were considered. Of the three

¹ Whitepaper in Response to Spring 2005 IPR Action Item #1 for Project CU-0312 submitted 1 November 2005

possibilities, Redstone Arsenal was selected for meeting these criteria plus the added benefit of the site's proximity to ARA's Panama City, Florida office, which facilitated field support and operation, and minimized costs associated with travel and transporting equipment/supplies.

3.3 Test Site Description

Redstone Arsenal is located in the heart of the Tennessee Valley, in northern Alabama. The facility was built in 1941 to produce conventional chemical ammunition for use in World War II. For more than 40 years, Redstone has been the heart of the Army's rocket and missile programs. Dr. Werner von Braun and his German rocket experts developed the first ballistic missile; this led to the establishment of NASA's Marshall Space Flight Center in 1960. Today, Redstone is home to the U.S. Army Aviation and Missile Command (AMCOM), the Space and Missile Defense Command, numerous Program Executive Offices (PEO), and major components of the Defense Intelligence Agency and the Missile Defense Agency. Also located here are numerous tenant and satellite organizations. "Team Redstone's" mission is to perform basic and advanced weapons system research and development, placing the right missile and aviation systems with the troops, keeping them ready to fight, providing weapon systems, services and supplies to our allies, to manage weapon systems such as the Cobra and PATRIOT, and to support project managers within the program executive office structure.

Site OU-10 at Redstone Arsenal has approximately 400 monitoring or extraction wells with perchlorate contamination ranging from very low parts per billion up to 10,000 ppb. Many of these wells also have VOC contamination, primarily TCE, which was considered prior to well selection. Redstone Arsenal has assisted with site selection for the demonstration by providing ARA with perchlorate, TCE, and pump rate data for groundwater monitoring wells. Well selection guidelines also include having the minimum TCE contamination possible while maintaining the capability to pump at a sufficient rate for the demonstration system. Existing infrastructure was also a consideration as the demonstration system requires power and communication lines. Figure 3-3 shows the candidate monitoring wells, with perchlorate and TCE concentrations, considered for this demonstration. Although the monitoring wells have perchlorate contamination that meet concentration requirements, they did not have the production capacity needed. ARA visited Redstone Arsenal on April 1, 2005 to discuss site selection and demonstration issues with Redstone personnel. During this visit a number of extraction wells were identified that met the demonstration requirements. Of the locations identified, well RS498 was selected as the primary demonstration well, with RS497 and RS496 identified as secondary choices. These well locations, relative to one another, and the perchlorate plume are shown in Figure 3-4.

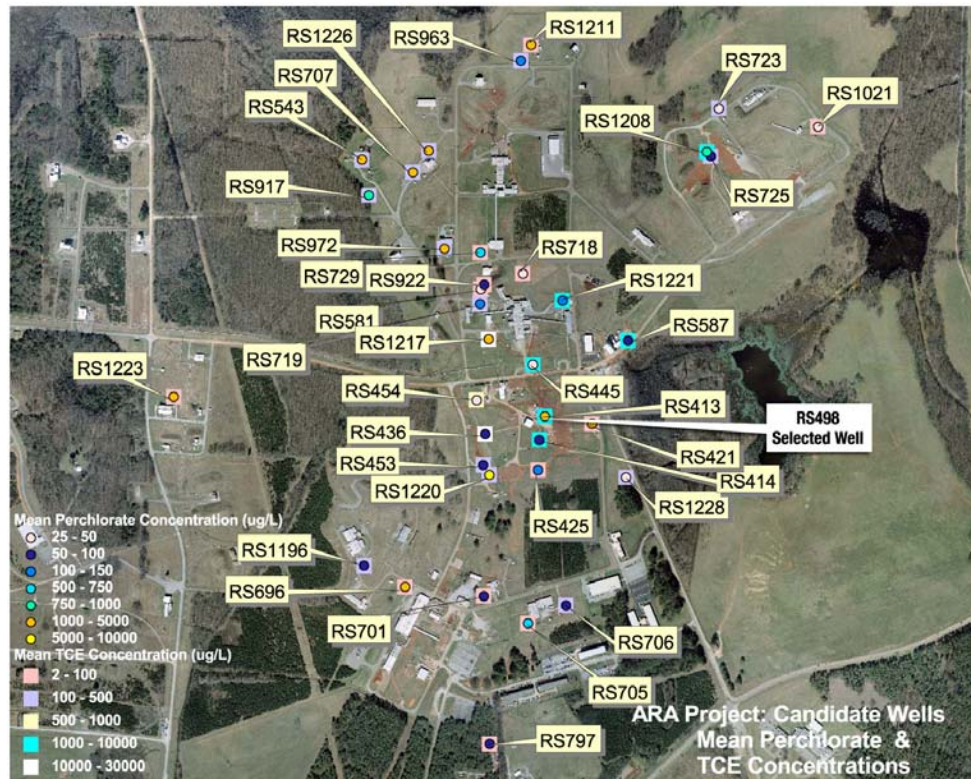


Figure 3-3. Wells Available for Demonstration at Redstone Arsenal

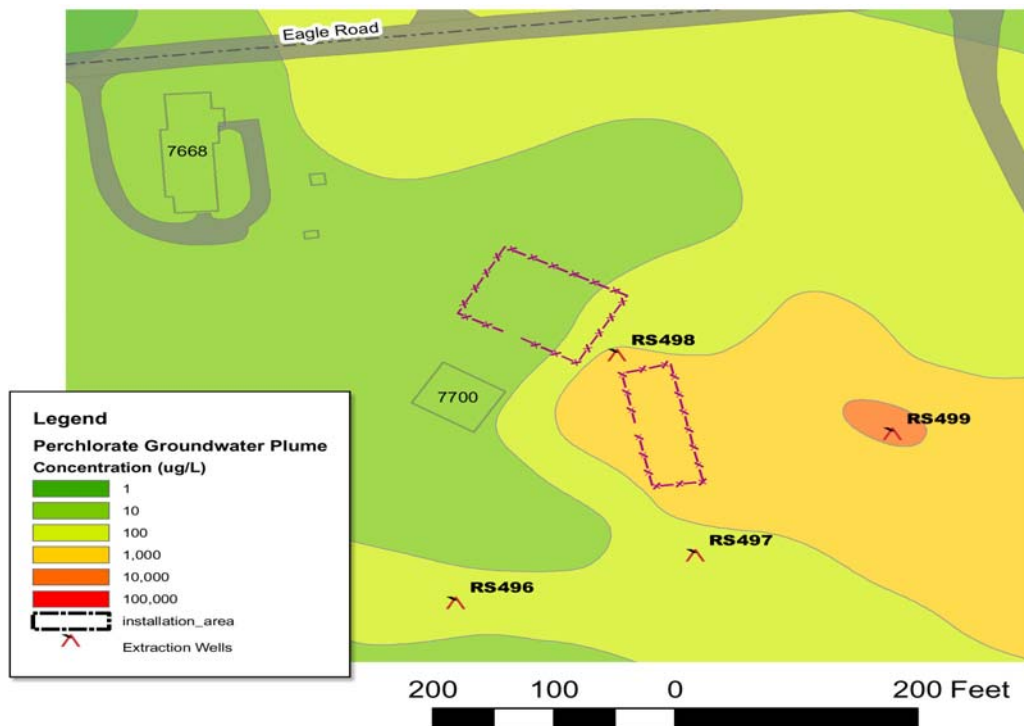


Figure 3-4. Candidate Wells Selected for Demonstration

3.4 Pre-Demonstration Testing and Analysis

Since the demonstration is evaluating how effective ARA's WBA resin ion exchange process removes perchlorate from groundwater, perchlorate data of well RS498 were gathered starting from December 2000. Anion concentrations of nitrate, sulfate, and chloride were also determined on April 2005. These data were used to determine operation parameters and predict the duration of test periods before breakthrough.

For baseline comparisons during each test period, RS498 was sampled at the conclusion of the five test periods, along with treated effluent. Sampling parameters included pH, alkalinity, anions (chloride, nitrate, and sulfate), perchlorate, VOCs, and TDS.

3.5 Testing and Evaluation Plan

3.5.1 Demonstration Installation and Start-Up

Well RS498 was selected for the demonstration (Figure 3-5). RS498 is a 6-inch well installed in 1995. The well is rated at 25-30 gpm production, which provided more than enough groundwater for this demonstration (maximum flow rate: 0.21 gpm). There was easy access from a road to this well and it was surrounded by level ground for the demonstration trailer.

The ion exchange pilot treatment system was fabricated at ARA's Panama City Research Facility. The system was installed in an eight feet by twenty feet enclosed trailer and a series of functional tests were performed prior to field mobilization. The enclosed trailer was configured to provide breakered power, climate control, and protection from the elements while in the field.

A phone line was installed at the site on 6/16/05 for accessing data using a web-based data acquisition system. On this same date, the well-pump was installed (Figure 3-5) as well as a disconnect box to provide power for the demonstration trailer. The demonstration trailer was hauled to Redstone Arsenal on 6/20/05. During this week, the system was prepared for the demonstration and the field monitor was integrated. Arrangements were made for site access and on-site consultants were trained to sample and monitor the system. The first test period of the demonstration was initiated on 6/23/05.

Site visits were conducted at least three days per week to inspect the system, sample, record data, and prepare dilute acid and/or caustic solutions and re-fill reservoirs for the pre- and post-treatment units. At the end of each test period, the system was sampled and the flow was suspended to remove the spent lead column, transition the lag column to the lead column position and configure a regenerated column as the lag column. Maintenance of the ion exchange system during this flow suspension also included replacing the in-line groundwater filter, cleaning and calibrating pH electrodes, and calibrating flow of the digital flow meter. Following maintenance and any adjustments, the flow was initiated for the new test period. Spent columns from each test period were transported to ARA's laboratory in Panama City, FL for regeneration.



Figure 3-5. Well RS498 with Well-Pump and Tank

The field monitor was fabricated at ARA's New England Division in Vermont and laboratory tests were conducted simulating predicted operations in the field. The field analyzer was configured in a fiberglass NEMA enclosure and installed in the test trailer at Redstone Arsenal during system mobilization (Figure 3-6). Modifications to the reservoirs that were designed to supply the monitor with de-gassed sample were accomplished on-site and the monitor was placed in operation. Three initial failures (two valves and one pump) occurred as a result of unforeseen software problems. Another failure occurred when the program crashed. During this program failure, the FMI pump was left running and the pump emptied the de-ionized water reservoir. As a result, the pump shaft was damaged.

In the two other cases, program crashes caused method steps to be missed resulting in the pump attempting to force fluid through a "dead-headed" three way valve, which then burst from over-pressure. Therefore, the monitor did not operate long enough remotely to generate useful data. It was returned to ARA-NED for trouble-shooting.

Once the monitor was returned to ARA-NED, data was collected by running the monitor manually (i.e. starting each run independently). Realistic conditions were set up with daily de-ionized water Blank and Standard and surrogate samples. Surrogate water was created by adjusting daily well water samples to pH 4.0 with sulfuric acid and spiking to perchlorate concentrations that were typical of samples taken from lead and lag (effluent) columns. Surrogate "effluent" and early-stage "lead" were run with 500-mL sample volumes and late-stage "lead" samples were run with 12-mL volumes.

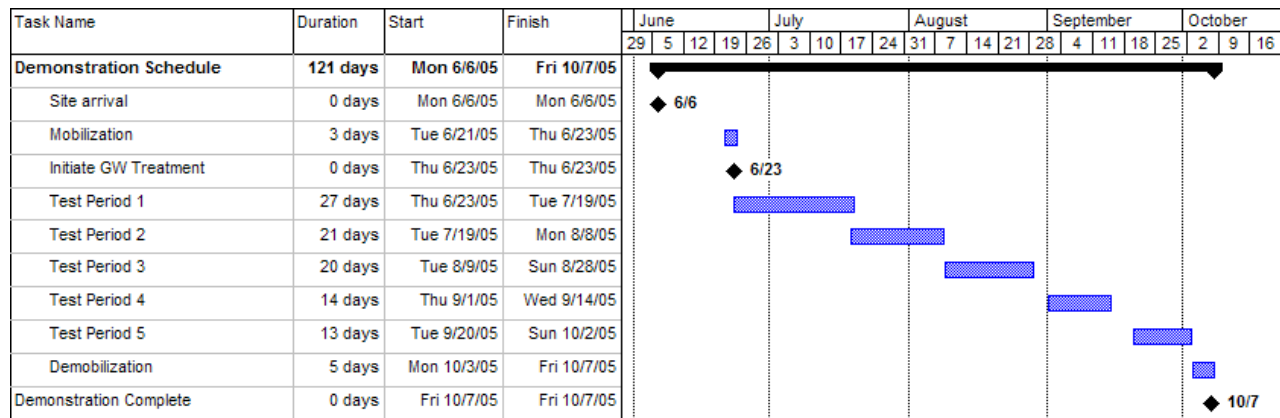


Figure 3-6. Final prototype as installed at Huntsville.

3.5.2 Period of Operation

Testing at Redstone Arsenal was conducted in five test periods. The dates and duration of the five test periods are listed in Figure 3-7.

Figure 3-7. Duration of each Test Period



3.5.3 Amount /Treatment Rate of Material to be Treated

The volume of water treated during each test period and the total volume of water treated is listed in Table 3-5.

Table 3-5. Amount of Water Treated

Test Period	Flow Rate		Volume Treated	
	BV/hr	gals/hr	Bed Volumes	Gallons
1	12	6.3	7483	3954
2	12	6.3	6091	3218
3	12	6.3	5018	2652
4	18	9.5	6421	3393
5	24	12.7	7913	4181
TOTAL			32926	17398

3.5.4. Residuals Handling

Effluent from the WBA resin ion exchange demonstration was collected in a 5000-gallon conical bottom tank located in building 7700. This tank has an inlet to Redstone Arsenal's VOC treatment system. Once the level in the tank reached the appropriate height, the effluent from the ion exchange system was treated to remove TCE. Treated water was stored in a 2500-gallon tank until analytical results confirmed that the effluent met requirements for discharge.

The waste generated by the field monitor, including acetone and xylene, was stored in a waste container. Because the field monitor did not operate, less than five gallons of hazardous waste was taken to a disposal center at the conclusion of the demonstration.

Spent ion exchange columns were removed from the system and transported to ARA's Panama City facility for regeneration. Spent regenerating solutions were collected and used in bench scale perchlorate destruction tests. Effluents from these tests were disposed under ARA's municipal discharge agreement after analyses confirming that perchlorate was destroyed/removed.

3.5.5 Operating Parameters for the Technology

The pilot demonstration system was operated in a continuous flow manner. The system, described in detail in Section 2.1, was designed with a data acquisition unit that was remotely accessed via the internet. This allowed remote monitoring of key operating parameters including pH, pressure, flow rate, and pH and temperature of influent and column effluents.

The system was inspected and sampled by project personnel at least three times per week. Inspection and sampling typically required an hour per site visit. At the end of each test

period, column change outs required two project personnel to perform final sampling, column reconfigurations, system maintenance (described in section 3.5.1), and start up.

3.5.6 Experimental Design

ARA conducted laboratory and field experiments to evaluate WBA resin technology using the selected resin (Purolite D4170). Laboratory experiments were conducted to determine pH influences on the selected WBA resin and to characterize and optimize operational conditions for the field demonstration. Laboratory results were also used to predict breakthrough times based upon influent anion concentrations and flow rates. Descriptions of laboratory experiments and field testing conditions are summarized in Tables 3-6 and 3-7, respectively. Detailed descriptions and summaries of the results for laboratory, field, and regeneration experiments are provided in Appendix A Section 4.0.

Laboratory Experiments

Table 3-6. Laboratory Experiments

Experiment	Type (Batch or Flow)	Objective(s)	Runs	Comments
Titration	Batch	<ul style="list-style-type: none"> Determine effects of pH on exchange capacity of the resin 	1	8 titration end-points
Isotherm	Batch	<ul style="list-style-type: none"> Determine perchlorate sorption in a matrix similar to groundwater at demonstration site Use results to predict perchlorate breakthrough based on concentration in influent 	4	7-9 data points per isotherm
Column	Flow	<ul style="list-style-type: none"> Determine resin treatment capacity Demonstrate repeated loading and regeneration cycles Attain accurate material balance data 	8	4 accelerated loading (450-5,000 BVs) 4 breakthrough (10,000 BVs)

Field Experiments

Three columns, identified as C1, C2, and C4, were used throughout the demonstration. Each column had an internal diameter of 2.049-inches and was packed with 36-inches of Purolite D4170 resin. The resin bed volume was calculated to be 1.945 liters. Prior to initiating the demonstration, each column was preconditioned to minimize any uncharacteristic behavior that may result from using virgin resin. Preconditioning consisted of protonating, loading with perchlorate using a surrogate water, regenerating, and protonating in preparation for treating groundwater at the demonstration site.

There were five test periods during the demonstration at Redstone Arsenal. Key operating parameters for each test period, including flow rate, column identification for the lead and lag positions, and the post treatment conditions, are provided in Table 3-7.

Table 3-7. Operating Conditions during each Test Period

Test Period	Flow Rate (BV/hour)	Flow Rate (gpm/ft ³)	Lead Column ID	Lag Column ID	Caustic Conditions
1	12	1.5	C1	C2	Set point at 6.8; air pump controlled with caustic addition.
2	12	1.5	C2	C4	Set point at 7.4; air pump on continuously.
3	12	1.5	C4	C1	Set point at 7.4; air pump on continuously.
4	18	2.25	C1	C2	Set point at 6.8; air pump on continuously.
5	24	3.0	C2	C4	Set point at 6.8; air pump on continuously.

Regeneration & Residual Experiment.

Objectives for regeneration and residual treatment experiments are summarized in Table 3-8. Results are provided in Appendix A Section 4.0.

Table 3-8. Objectives for Regeneration and Residual Treatment Experiments

Experiment	Type (Batch or Flow)	Objective(s)	Runs
Regeneration	Batch & Flow	<ul style="list-style-type: none"> Evaluate regeneration procedures for effectiveness Determine perchlorate recoveries 	5
Superloading	Flow	<ul style="list-style-type: none"> Evaluate as a perchlorate removal process for spent regenerant Evaluate superloading as a zero-discharge procedure 	1
Biodegradation	Flow	<ul style="list-style-type: none"> Evaluate as a perchlorate destruction process for spent regenerant 	1

Two approaches were evaluated for regenerating the spent ion exchange resin. These were single-pass regeneration and batch regeneration. The more conventional, single-pass approach (Figure 3-8) was used to regenerate the spent column from the first test period. The regeneration solution was prepared by adding caustic to three bed volumes of water, which was passed over the resin at a flow rate of 2 bed volumes per hour. The spent regenerant was collected for analysis and perchlorate destruction studies using the scavenger approach. For complete regeneration using the single-pass approach, excess caustic was required (50%) and it was difficult to minimize the volume of spent regenerant.

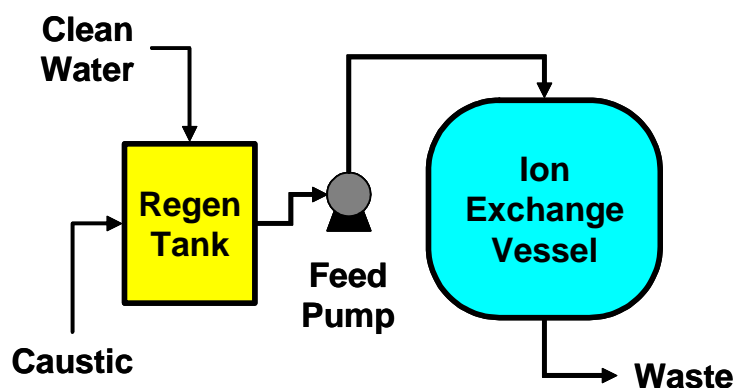


Figure 3-8. Single-Pass Regeneration

A batch regeneration approach was also conducted (Figure 3-9). A stoichiometric amount of caustic plus 10% excess was added to three bed volumes of potable water to prepare the regenerating solution. This solution was circulated over the resin bed until the pH of the column effluent was greater than twelve. The solution was drained from the column and collected for analysis and perchlorate destruction studies. The batch regeneration approach enabled complete regeneration while minimizing caustic consumption and spent regenerant volume. Batch regeneration was used for all remaining tests, and the spent regenerant solutions generated were collected for perchlorate destruction tests using biodegradation. Following regeneration, regardless of the approach, a rinse was conducted to adequately remove residual perchlorate from the regenerated resin bed. This was done to eliminate bleed at the start up of the next cycle. The rinse water was collected, analyzed, and used to dilute spent regenerant prior to the biodegradation study.

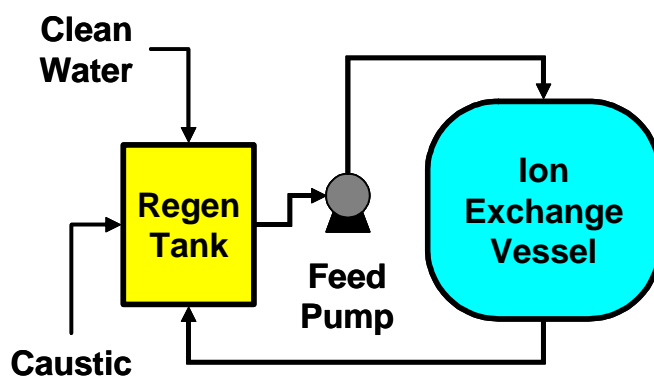


Figure 3-9. Batch Regeneration

The scavenger apparatus consisted of four, 15-mm diameter columns in series packed with 90cc of Purolite A-600, a strong base anion resin (Figure 3-10). The spent regenerant from the first test period was passed over the columns loaded with Purolite A-600 at a flow rate of 10 bed volumes per hour. Effluent from each of the four columns

was collected every hour (every 10 bed volumes) until completion. The results, plotted in Figure 3-1 located in Section 3.1.A.6, show that perchlorate was completely removed from the spent regenerant by the first two scavenger columns.

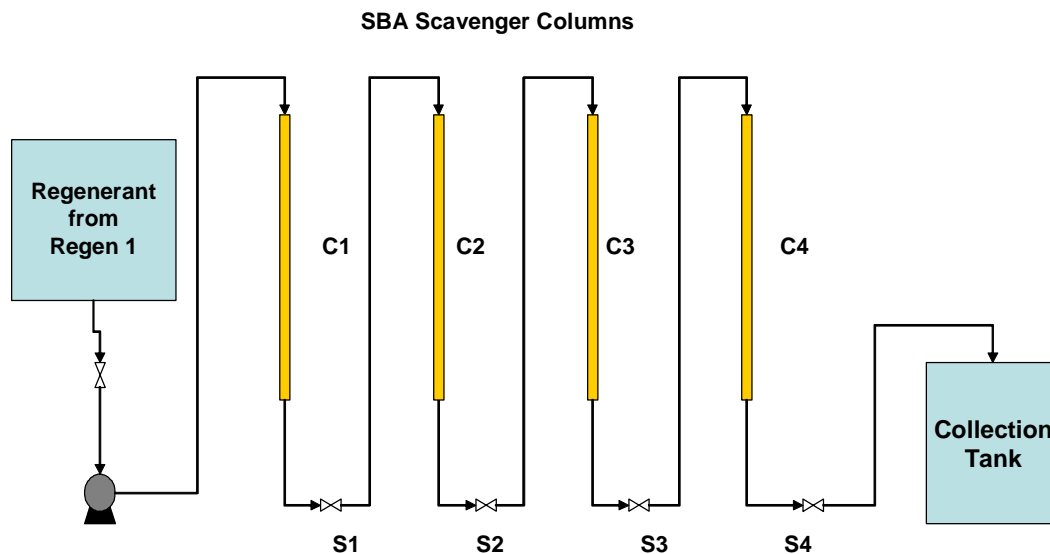


Figure 3-10. Scavenger Apparatus

Biodegradation studies were also conducted to evaluate perchlorate destruction in spent regenerant. The apparatus consisted of two, 2.5-liter, continuously stirred tank reactors (CSTR) in series. A carbon-based nutrient source (desugared molasses) was added to the first reactor and the pH of both reactors was controlled. Spent regenerant solutions from test periods 2 through 5 were combined, diluted with spent rinse water to reduce the total dissolved solids (~1%), and neutralized prior to biodegradation. The average perchlorate concentration of the feed water during biodegradation testing was 600 mg/L. Biodegradation of the diluted spent regenerant was conducted over 33 days during which the perchlorate was reduced to below the method detection limit for this matrix using EPA 314.0. There was a three-day period during which perchlorate was not reduced to below the detection limit in the second stage reactor. This was caused by insufficient nutrient (desugared molasses) addition. After adjusting the nutrient level, perchlorate was again reduced to below the detection limit.

3.5.7 Sampling Plan

As part of the demonstration plan for this effort, a Quality Assurance Project Plan was developed and utilized to ensure that samples were collected and analyzed properly. This plan was developed based upon EPA guidance and ARA's experience in operating ex situ groundwater systems. The plan is included as Appendix B. The only exception to this plan was regarding perchlorate analysis using the online field monitor. Software and mechanical failures prevented the online field monitor from remote operation. As a result, the field monitor was never used to analyze groundwater and column effluent samples for perchlorate as originally planned. All perchlorate analyses were conducted using EPA Method 314.0.

Field Sampling

There were five locations sampled during the field demonstration. These sampling points consisted of ball-valves that were plumbed in an appropriate location for representative sampling. Each valve was clearly labeled to mitigate confusion and/or mislabeling of sample bottles. These locations are identified and described in Table 3-9.

Table 3-9. Sampling Locations

	Sample ID	Valve Location
1	Pretreatment	Following pretreatment mix tank; before lead column
2	Lead Column	Following lead column; before lag column
3	Lag Column	Following lag column; before post treatment tank
4	Post Treatment	Out of post treatment tank; before discharge to holding tank
5	Groundwater	At well head

During the field demonstration, samples were collected from pre- and post-treatment units, and lead and lag column effluents at least three times per week by ARA personnel or technicians trained by ARA. The following sampling procedure was followed: "Label sample bottles with the date, time (military), sample ID (including column ID), and your initials. For example, 6/24/05 14:30, Lead (C1) AD. Before collecting the sample, flush the sample valve by collecting 20-25 milliliters in a beaker. Then collect the sample into the labeled sample container." Samples were stored according to Table 3-10.

Table 3-10. Sample Parameters, Volume, Preservative Requirements and Hold Times

Parameter	Matrix	Method	Volume	Container & Preservation	Hold Time
Perchlorate	Aqueous	EPA 314.0	100 ml	HDPE, Cool 4°C	28 days
Anions	Aqueous	EPA 300.1	100 ml	HDPE, Cool 4°C	28 days
Turbidity	Aqueous	SM 2130B	100 ml	HDPE, Cool 4°C	48 hrs
Color	Aqueous	SM 2120B	50 ml	HDPE, Cool 4°C	48 hrs
Hardness	Aqueous	SM 2340	100 ml	HDPE, Cool 4°C, pH<2, HNO ₃	6 months
Alkalinity	Aqueous	SM 2320B	100 ml	HDPE, Cool 4°C	14 days
Conductance	Aqueous	SM 2520	100 ml	HDPE, Cool 4°C	28 days
pH	Aqueous	SM 4500	5 ml	N/A	Immediate
Solids (TS/TDS)	Aqueous	SM 2540	100 ml	HDPE, Cool 4°C	7 days
Metals (Ca, Cu, Fe, Mg, Mn, K, Na, Zn)	Aqueous	SM 3125	200 ml	HDPE, pH<2, HNO ₃	6 months
VOCs	Aqueous	EPA 8260	40 ml	glass, Cool 4°C, pH<2, HCl, 0.25% Na ₂ S ₂ O ₃	14 days

Samples were analyzed for perchlorate and anions including nitrate, sulfate, and chloride using EPA Methods 314.0 and 300.1. The well and the post treated effluent were sampled at the end of each test period for these anions, TCE, and a series of general physical and mineral analyses. A sampling summary is provided in Table 3-11.

Table 3-11. Sampling Summary for ESTCP Pilot Demonstration

Parameter	Sample Point	Sample Frequency	Method	#Samples collected*
Perchlorate	1,2,3,4	Biweekly Minimum	Lab	184
Anions	1,2,3,4	Biweekly Minimum	Lab	214
pH	1,2,3,4	Continuous	Online/Field	---
General Physical/Mineral	4 and 5	Test Period End	Lab	10
VOC	4 and 5	Test Period End	Lab	10

*These numbers do not include duplicates or QA/QC samples collected and analyzed in accordance with the QAPP.

Operational data such as pH, flow, and pressure were collected and stored by a data acquisition system. These data along with acid and caustic tank levels were recorded in a log notebook by a technician on each sampling day. The technician would also call ARA personnel and provide the data while on-site. These data were recorded in spreadsheets and reviewed to ensure the system was operating as expected.

Laboratory Sampling

During regeneration tests, anion analyses (perchlorate, sulfate, nitrate, and chloride) were conducted on each bed volume of spent caustic regenerating solution using EPA Methods 314.0 and 300.1. The anion results were used to determine regeneration effectiveness and anion composition of the regeneration solution before perchlorate destruction tests were initiated.

Two processes were evaluated for perchlorate destruction tests conducted on spent regenerant solutions. These include superloading and biodegradation. During superloading tests, sampling was conducted on each bed volume passed through superloading resin. During biodegradation tests, two bench-scale (2.5 liters) flow reactors were configured in series. The pH, temperature, oxidative/reduction potential, and nutrient and caustic consumption were recorded daily for each reactor. Each reactor was sampled daily for perchlorate analysis using EPA Method 314.0. Other anion analyses (nitrate, sulfate, and chloride) was conducted at least biweekly using EPA Method 300.1. A sampling summary for regeneration and residual treatment tests is provided in Table 3-12.

Table 3-12. Sampling Summary for Regeneration and Residual Treatments

Process	Parameter	Sample Frequency	Method	#Samples Collected
Regeneration	Perchlorate	Each BV	EPA 314.0	56
	Anions	Each BV	EPA 300.1	55
	pH	Each BV	SM 4500	36
Superloading	Perchlorate	Each BV	EPA 314.0	37
	Anions	Each BV	EPA 300.1	36
	pH	Each BV	SM 4500	0
Biodegradation	Perchlorate	Daily	EPA 314.0	95
	Anions	Weekly	EPA 300.1	69
	pH & ORP	Daily	Online	Continuous

A complete sampling and analysis plan detailing analytical techniques, QA/QC requirements and sampling procedures is included in the QAPP, attached as Appendix B. QA/QC results are provided in Section 4, Table 4-3.

3.5.8 Demobilization

The system was sampled the final time and shut down on 10/3/05. Demobilization occurred from 10/5 – 10/7 during which the site was returned to conditions prior to the demonstration (phone line disconnected, well pump removed, electric box and cables removed, etc). Following a site inspection by Redstone Arsenal personnel, the demonstration trailer was hauled off the site on 10/7/05. Any remaining effluent stored in the 5000-gallon conical bottom tank was treated for VOCs. The water was discharged following analyses verifying that discharge requirements were met.

3.6 Selection of Analytical/Testing Methods

The critical parameter for this study was the analysis of anions – specifically perchlorate – in groundwater. The perchlorate field monitor was designed to analyze daily perchlorate concentrations for the pretreated groundwater and ion exchange effluents using a method developed by ARA (described in the Appendix B). However, software and hardware failures described in 3.5.1 prevented remote operation of the monitor. Instead, daily samples of pretreated groundwater and column effluents were analyzed using EPA Methods 314.0 and 300.1 for perchlorate and anions (chloride, sulfate, and nitrate) during the first two weeks of the demonstration. After the first two weeks, samples were analyzed at least three days per week for perchlorate and anions. Additional analytical measurement including pH, conductivity, solids, metals, color, turbidity, hardness, alkalinity, and VOCs were performed using the appropriate Standard/EPA method. A listing of analytical procedures is provided in Table 3-13 with detailed descriptions of the analytical methods used during this demonstration included with the QAPP, attached as Appendix B.

Table 3-13. Analytical Procedures used during the Demonstration

Parameter	Matrix	Lab	Method	Method Type
Perchlorate*	Aqueous	ARA	EPA 314.0	Ion Chromatograph
Perchlorate*	Aqueous	ARA	Online monitor	SPE/Colorimetric
Anions	Aqueous	ARA	EPA 300.1	Ion Chromatograph
pH	Aqueous	ARA	SM 4500	Electrometric
**General Physical/ Mineral Scan	Aqueous	ELAP Certified	Various	Various
VOCs	Aqueous	ELAP Certified	EPA 8260	Gas Chromatograph – Mass Spec

*Notes: Critical compound for performance validation is ClO_4 . **General physical scan includes pH, color, turbidity, total alkalinity, total hardness, conductance, TDS, calcium, copper, iron, magnesium manganese, potassium, sodium, and zinc.

3.7 Selection of Analytical/Testing Laboratory

Samples were analyzed for perchlorate, other inorganic anions, and basic water quality parameters at ARA's in-house laboratory. Samples taken at the end of each test period were split and shipped to Associated Laboratories in Orange, California for an external confirmatory analysis for perchlorate as well as other general mineral and physical analyses. The address of each laboratory is listed below.

In-House Analyses

Applied Research Associates, Inc.
430 West 5th Street, Suite 700
Panama City, Florida, 32401
Phone #: 850-914-3188

External Analyses

Associated Laboratories
806 North Batavia
Orange, CA 92868
Phone #: 714-771-6900
ELAP Certification #- 1338

4. Performance Assessment

4.1 Performance Criteria

Performance criteria and a description of what makes the criteria a success are provided in Table 4-1.

Table 4-1. Performance Criteria

Performance Criteria	Description	Primary or Secondary
Contaminant Reduction	Removal of perchlorate from ground water via pump-and-treat ion exchange process to below the MCL	Primary
Resin Regeneration	Effective and efficient regeneration of WBA resin enabling reuse	Primary
Process Waste	<ul style="list-style-type: none"> • Small volume of spent regenerating solution (<0.1%) • Biodegradability of spent regenerating solution • Concentration of perchlorate in spent regenerating solution 	Primary Primary Primary
WBA Resin Capacity	G/W treatment capacity	Primary
Treatment Rate	Acceptable performance at 1.5 gpm per ft ³ of resin	Primary
Pretreatment pH	Effective operational pH	Secondary
Reliability	<ul style="list-style-type: none"> • Perchlorate leakage • pH control • CO₂ management • Resin useful life 	Primary Secondary Secondary
Ease of Use	<ul style="list-style-type: none"> • Degree of automation • Labor requirement • Skill level requirements 	Secondary
Versatility	<ul style="list-style-type: none"> • G/W, drinking water, or wastewater • Wide range of perchlorate concentrations 	Secondary
Maintenance	<ul style="list-style-type: none"> • Frequency • Complexity • Cost 	Secondary
Scale-Up Constraints	<ul style="list-style-type: none"> • Representative bed depth • Representative flow rate • Pre/Post treatment scale 	Secondary
Field Monitor Operation	<ul style="list-style-type: none"> • MDL of 1 ppb • Precision \pm 25 % • Dynamic range 	Primary
	<ul style="list-style-type: none"> • Ease of use 	Secondary

4.2 Performance Confirmation Methods

The effectiveness and/or success of this demonstration was measured against the performance objectives detailed in Section 4.1. To ensure that proper data collection and analyses techniques were followed, the Quality Assurance Project Plan (QAPP) included in the approved Demonstration Plan was followed and is attached as Appendix B. Table 4.2 summarizes the expected performance, performance confirmation methods, and the actual confirmation methods used to evaluate demonstration performance.

Table 4-2. Expected Performance and Performance Confirmation Methods

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Methods	Actual (post demo) Future
PRIMARY CRITERIA (Performance Objectives)			
Contaminant Reduction	Remove ClO_4 with IX process to $\leq 5\text{ppb}$	Online monitor & EPA method 314	Perchlorate concentration in effluent analyzed by EPA Method 314.0
Resin Regeneration	Effective regeneration of resin. +90% recovery of ClO_4 loaded onto resin	Mass balance feed/effluent with data from online monitor & EPA method 314	Mass balance calculations using perchlorate concentration data for feed and effluent analyzed by EPA Method 314.0
Process Waste	Generate $\leq 0.1\%$ spent regenerant volume of total volume treated	Collect and measure spent regenerant volume	Collected and measured spent regenerant volume and compared to volume treated
	Biodegradability of spent regenerating solution	Degrade ClO_4 in solution process to $\leq 5\text{ppb}$. EPA 314	Perchlorate concentration in reactor effluent analyzed by EPA Method 314.0
	Concentration of ClO_4 in regenerating solution	Remove ClO_4 in regenerating solution to $\leq 5\text{ppb}$. EPA 314	Perchlorate concentration in treated regenerating solution analyzed by EPA Method 314.0
Perchlorate Capacity of resin	$\geq 30\text{ meq/L}$	Mass balance feed/effluent with online monitor & EPA314	Calculated using perchlorate concentrations of feed & effluent analyzed by EPA Method 314.0
Treatment Rate	$\geq 1.5\text{ gpm/ft}^3$	Flow rate monitor/totalizer	Verified flow rate using flow rate monitor (total flow) over time between sampling

**Table 4-2. Expected Performance and Performance Confirmation Methods
Continued**

Reliability	Perchlorate leakage	Analysis at flow rates > 1.5 gpm/ft ³	Analyzed for column effluent for perchlorate using EPA Method 314.0 during periods before breakthrough occurrence
Field Monitor Operation	MDL ≤ 1ppb	Statistical analysis of results of lowest standard	Statistical analysis of results of lowest standard
	Precision ± 25%	Statistical analysis of duplicates	Statistical analysis of duplicates
SECONDARY CRITERIA (Performance Objectives)			
Pretreatment pH	Effective Operational pH	pH varied from 4.0 baseline, ClO ₄ removal measured	pH varied from 4.0 baseline, ClO ₄ removal measured
Reliability	pH Control	Online pH monitor recorded with DAS	Recorded pH readings at each sampling and also every 15 minutes with the DAS
	CO2 management	Influent/Effluent alkalinity measurement	Analyzed alkalinity of groundwater and post treated effluent at conclusion of each test period.
	Resin useful life	ClO ₄ removal capacity measured after load/regenerating cycles	Determined capacity of resin after each test period. Normalized and compared to all five test periods.
Versatility	G/W, drinking water application, wide ClO ₄ treatment range	Remove ClO ₄ with IX process to ≤ 5ppb from feed of 1,000 ppb	Determine perchlorate concentration data for pretreated groundwater and column effluents analyzed by EPA Method 314.0
Maintenance	Frequency, complexity, cost	Experience and monitor from demonstration operation	Maintained log books recording sampling and maintenance activities
Scale-Up Constraints	Representative bed depths, flow rates, pre/post treatment scale	System design with scale up considerations, monitor from demonstration	

Many of the performance criteria were based on comparing perchlorate concentrations of groundwater or pretreated groundwater to column effluents. For this reason, care was taken to ensure that sampling and analysis of these samples was compliant with the attached QAPP (Appendix B). Quality control results for perchlorate analyses are listed in Table 4-3. At the end of each test period, split samples were sent to a certified laboratory for analyses. The perchlorate results of each laboratory are listed in Table 4-4. The mean relative percent difference is 9.9%.

Table 4-3. Perchlorate Quality Control

Analysis Date	Accuracy (% Recovery)	Precision (RPD)	CCAL (%)	Method Blank
7/1/2005	89.6	15.0	3.8	<4 µg/L
7/6/2005	104.2	2.9	12.0	<4 µg/L
7/13/2005	104.7	3.8	2.9	<4 µg/L
7/25/2005	103.6	0.9	0.3	<4 µg/L
7/28/2005	88.9	2.2	6.8	<4 µg/L
8/4/2005	95.5	1.0	1.1	<4 µg/L
8/10/2005	98.7	5.1	10.3	<4 µg/L
8/12/2005	85.4	1.2	13.8	<4 µg/L
8/26/2005	91.6	10.5	1.7	<4 µg/L
9/2/2005	107.0	3.6	2.5	<4 µg/L
9/13/2005	99.8	4.0	3.2	<4 µg/L
9/16/2005	123.0	8.8	0.8	<4 µg/L
9/29/2005	97.9	2.5	2.4	<4 µg/L
10/4/2005	101.6	1.1	1.5	<4 µg/L
10/5/2005	98.1	1.0	5.0	<4 µg/L

Table 4-4. Split Samples Analyzed for Perchlorate

Test Period		1		2		3		4		5	
Sampling Date		7/19/2005		8/9/2005		8/29/2005		9/15/2005		10/3/2005	
Analyst	Unit	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
ARA	µg/L	1504	<4	1352	9.28	1631	<4	2386	<4	2112	<4
Certified Lab	µg/L	1479	<4	1570	10.8	1710	<4	1929	<4	2079	<4
RPD	%	1.7	N/A	14.9	15.1	4.7	N/A	21.2	N/A	1.6	N/A

4.3 Data Analysis, Interpretation and Evaluation

The performance objective results were evaluated against the expected performance metric to determine success of the demonstration (see section 3.1). The primary operating parameter that influences the WBA anion exchange process is the pH of the influent. Based upon laboratory experiments (see Appendix A Section 2.0), the optimal operating pH was identified as 4.0. The pretreatment pH control unit was set to control influent groundwater to 4.0. Operational data recorded during the demonstration indicate the pH of the influent water and the column effluents remained close to the controlled pH. The pH meters used to record the pH were calibrated at

each column transfer as part of system maintenance. The average pH of the influent and column effluents and the standard deviation are listed in Table 4-5.

Table 4-5. Average Operating pH of Influent and Column Effluents

Location	Average pH	Standard Deviation
Pretreated Groundwater	3.92	0.15
Lead Column Effluent	3.88	0.38
Lag Column Effluent	3.98	0.45

Another important operating parameter is the flow rate. It was important to determine if operating the system at higher flow rates would lead to perchlorate leakage. Operational flow rates during the demonstration were 12 BV/hr, 18 BV/hr, and 24 BV/hr (1.5, 2.25, and 3.0 gpm/ft³, respectively). As described in section 3.1.A.2, there was perchlorate leakage due to insufficient rinsing after resin regeneration. However, once the rinse procedure was corrected, no perchlorate leakage occurred even at the higher treatment rates of 2.25, and 3.0 gpm/ft³ (see Appendix A Section 3).

Project performance results were compared as a low-cost alternative to existing pump and treat processes for perchlorate remediation. Therefore, this technology was compared to existing ion exchange technologies being used primarily to treat drinking water. These technologies include regenerable ion exchange processes that use salt as the regenerating agent such as the Calgon ISEP process and conventional lead-lag processes. A cost comparison is provided in Section 5.3 and key performance benefits compared to brine regenerable SBA resin are listed below:

- **Low O&M Cost.** \$70 to \$85 per acre-foot compared to \geq \$200 per acre foot for SBA processes
- **Low Effluent Volume.** Less than 0.06% of treated water. 50X more efficient than regenerating with brine
- **Inexpensive Zero-Discharge Process.** Use of SBA scavenger resin. Allows for treated water to be discharged to sewer.
- **Standard Ion Exchange Equipment.** Fixed bed vessels, lead-lag configuration.
- **Use of Typical Water Treatment Chemicals for Regeneration.** NaOH, H₂SO₄, Na₂CO₃.

Issues associated with the use of WBA resin technology for perchlorate include:

- **Added Complexity.** Requires pretreatment and post treatment operations. Additional labor required for operation and maintenance.
- **Added Chemicals.** Acid and caustic must be added to the product water. Potential safety issues associated with handling acid and caustic.
- **Higher Capital Investment.** Additional unit operations and foot print.

5. Cost Assessment

5.1 Cost Reporting

5.1.1 Capital Cost

5.1.1.1 Application Scenarios

Cost data were developed for two different application scenarios: 1) Full-scale remediation of groundwater with properties similar to the groundwater treated during the demonstration test at Redstone Arsenal, and 2) Full-scale groundwater treatment system for groundwater containing low concentrations of perchlorate (<100 ppb) – typical for most drinking water applications. The design and operation of the WBA resin treatment systems are similar for each scenario with the exception of the disposition of the spent regenerating solutions. For remediating high concentrations of perchlorate (scenario #1), biodegradation is the least expensive solution. For most drinking water applications (scenario #2) use of a scavenger resin is a less expensive and simpler process.

5.1.1.2 Basis

The design and operating bases for the two scenarios are summarized in Table 5-1. A treatment rate of 2000 gpm was selected to permit direct comparison to single-use ion exchange systems that typically treat 1000 or 2000 gpm. Capital costs were derived from a budgetary cost estimate for a 400 gpm treatment system that was scaled to a 2000 gpm system. Capital cost for the biodegradation system used in the remediation scenario is based on a similar-sized commercial treatment system. It is assumed that the treated water alkalinity could be reduced to less than 5 mg/L for remediation scenarios.

Table 5-1. Summary of Design and Operating Bases

Parameter	Remediation	Drinking Water
Treatment rate, gpm	2000	2000
Bed volumes (BV) per hour	24	24
gpm/ft ³ of WBA resin	3	3
Groundwater Composition		
Perchlorate, mg/L	1.5	0.05
Bicarbonate Alkalinity, mg/L	150	150
Treated water composition		
Perchlorate, mg/L	<0.004	<0.004
Bicarbonate alkalinity, mg/L	N/A - 5	30
WBA resin treatment capacity, BV	6500	15,500
Regeneration solution	Biodegrade and discharge to sewer	Scavenge perchlorate and reuse or discharge to sewer
Biodegradation treatment rate, gpm	2.0 (or 0.1% of feed)	N/A
Scavenger resin capacity, meq/L	N/A	800

5.1.1.3 Major Equipment

Table 5-2 provides a summary of major equipment for both treatment scenarios.

Table 5-2. Major Equipment

Equipment Description	Remediation	Drinking Water	Approx. Unit/Pkg Cost
Tanks and Vessels			
Ion exchange vessels (2 trains) – 12' diameter	4	4	48,000
Regeneration and protonation tanks – 6000 gal	2	2	3,000
Regeneration rinse feed tank – 2500 gal	1	1	1,850
Acid and Caustic storage tanks – 6000 gal	2	2	6,630
Pumps			
Regeneration and protonation – 400 gpm	2	2	21,250
Acid feed for protonation and pretreatment	2	2	1,950
Caustic feed for regeneration and post treatment	2	2	2,700
Rinse/transfer	2	2	12,150
Instrumentation & Controls			
pH controllers	4	4	1,370
Level sensors/switches	4	4	1,500
Flow meters	3	3	2,500
Programmable logic controller and OIT (pkg)	1	1	17,240
Other			
WBA resin (lead & lag +10% margin) per ft ³	1466	1466	500
Biodegradation system, CSTR – 2 gpm (pkg)	1	N/A	850,000
Ion exchange scavenger 15 ft ³ transportable	N/A	4	7,500
Stripping tower	N/A	1	95,000

5.1.2 Operating and Maintenance Cost

5.1.2.1 Primary O&M Cost Components

The primary O&M cost components are acid and caustic consumed in pretreatment, post treatment, and regeneration operations. Sulfuric acid (H₂SO₄) is the least expensive and safest strong acid to use for pretreatment and for resin protonation after caustic regeneration. However, hydrochloric acid (HCl) may be used without major cost impact for treating low-alkalinity (<50 mg/L) groundwater, or for scenarios that result in infrequent regeneration (>5000 BV treatment capacity). Sodium hydroxide (NaOH) is the least expensive and most efficient caustic to use for resin regeneration. In addition, high concentrations of sodium salts that result from the regeneration process will not cause precipitation or scaling problems, which could be the case if other caustic compounds were used for regeneration.

Sodium hydroxide was used in the cost evaluation for post treatment neutralization, which is required to restore pH and residual alkalinity for drinking water applications.

Other caustic compounds, such as soda ash (Na_2CO_3) or calcite (CaCO_3), may be used for post treatment and may be less expensive and more efficient than sodium hydroxide for some applications. Use of soda ash and calcite for post treatment depends on treated water hardness and alkalinity requirements. Carbon dioxide stripping may not be required for low-alkalinity groundwater, or non-drinking water applications.

The WBA resin ion exchange treatment process is designed to eliminate the need for additional pumping operations. The cost for pumping water to the system is common to any pump and treat system and, therefore, was not included in this cost analysis. The power requirement for an air blower for the stripping tower is minimal for two reasons: 1) Stripping towers will only be required for certain, high-alkalinity drinking water applications, and 2) CO_2 is very easy to strip from water and can be stripped in natural draft systems. Therefore, a low air volume or blower power is required. The power requirement for controls and for the small acid and caustic pumps used in this process will also be minimal. The power required for regeneration pumps will be significant; however, these pumps will operate intermittently with an anticipated duty cycle of less than 25%. The average electrical power consumption is estimated to be no more than the equivalent of 10 horsepower or 20 kw-hr/acre-foot.

The cost of treating spent regenerating solution is included in the cost evaluation. For drinking water applications, this cost includes the cost for scavenger resin replacement and incineration. Scavenger resin vessels are small ($15\text{-}30\text{ ft}^3$), transportable vessels that will be leased from and serviced by a third party. Spent regenerating solution from large treatment systems ($>5000\text{ gpm}$), or from remediation of groundwater with high concentrations of perchlorate ($>500\text{ ppb}$), may be more economically treated using a CSTR anoxic biodegradation process.

A full-scale ion exchange process will be fully automated – being controlled by a PLC – and require little labor. However, some labor will be required for maintenance; collecting samples; monitoring the receipt of acid, caustic, and scavenger resin; monitoring and evaluating system performance; and monitoring resin regeneration (~once per month). Average labor requirement is estimated to be 10 hours per week.

Macroporus styrene divinylbenzene WBA resin can maintain performance for over five years in industrial applications that require daily regenerations. Regeneration frequency for drinking water and remediation applications are predicted to be no more than 15 to 30 times per year based on pilot performance. Therefore, WBA resin life for groundwater treatment applications is predicted to be seven years.

5.1.2.2 O&M Cost Basis

Table 5-3 provides a summary of the cost bases used for the major O&M costs. Chemical costs are based on quotes for bulk tank truck delivery to a southern California site. Scavenger resin cost includes disposal and servicing costs for Purolite A-530E or A-600 type resin. WBA resin cost is the current market price for commercially available Purolite D4170 resin. Biodegradation cost includes chemicals, nutrient, power, and

maintenance cost (but not labor) for a small CSTR treatment system sized to treat the effluent from a 2000 gpm ion exchange process.

Table 5-3. Material Cost Basis

Description	Cost
Sulfuric acid, 96-98%	\$0.05/lb
Sodium Hydroxide, 50%	\$0.15/lb
Scavenger resin service (replace, dispose, transport)	\$180/ft ³
Weak base anion resin	\$500/ft ³
Electricity	\$0.15/Kw-hr
Operator labor	\$60/hr
Biodegradation cost (ClO ₄ ⁻ dry basis)	\$2.00/Kg

Table 5-4 provides a summary of Capital and O&M cost for 2000 gpm remediation and drinking water treatment systems. The normalized cost basis is dollars per acre-foot (AF) of water treated. This is the most appropriate basis for comparing high flow rate remediation and drinking water treatment systems. One acre-foot is equal to 325,851 gallons of water.

Purchased equipment cost in Table 5-4 was derived from the equipment unit and package costs and the quantities provided in Table 5-2. The other components of capital cost: installation, instrumentation and controls, piping, electrical services, site work, service facilities, engineering, construction expenses, and other indirect costs were estimated as a percentage of the purchased equipment cost. This is an appropriate capital cost estimating procedure for order-of-magnitude estimates for new plants. Percentages were based on published factors (Plant Design and Economics for Chemical Engineers, Fifth Edition; Peters, Timmerhaus, & West) and factors used recently by an A&E who was consulted for a similar project. The percentages used also took into account the complexity and maturity of the unit operations involved. The biodegradation unit cost was based on a budgetary cost estimate provided by an A&E for a similar-size treatment system. The biodegradation unit cost includes all engineering, installation, and startup costs.

Operating costs were derived from the cost bases provided in Table 5-3. Labor hours were based on 20 hr/wk for drinking water applications and 40 hr/wk for remediation applications due to the addition of a biodegradation treatment system. Additional operating cost for the biodegradation system was added to include the cost of nutrient, chemicals, and electricity.

Table 5-4. Cost Summary

<i>Cost Category</i>	<i>Cost Sub Category</i>	<i>Cost Basis</i>	
		Remediation	Drinking water
Capital Costs	Purchased equipment cost*	325,000	450,000
	Purchased equipment installation	162,500	225,000
	Instrumentation and controls	97,500	135,000
	Piping	113,750	157,500
	Electrical services	48,750	67,500
	Site work	65,000	90,000
	Service facilities	162,500	225,000
	Engineering	146,250	202,500
	Construction expenses	130,000	180,000
	Other indirect	48,750	67,500
	Biodegradation Unit (installed)	850,000	N/A
	SUBTOTAL:	2,150,000	1,800,000
	Startup and testing	75,000	75,000
	Initial resin charge	733,000	740,500
	TOTAL CAPITAL COSTS:	2,958,000	2,615,500
Operating Costs	Labor**	62,400	31,200
	Consumables**		
	Sulfuric acid	51,920	50,120
	Sodium hydroxide	28,790	59,760
	WBA resin replacement	104,760	104,760
	Scavenger resin replacement		17,200
	Biodegradation unit operation	11,770	
	Electricity	9720	9720
	TOTAL OPERATING COSTS:	269,360	272,760
	Quantity treated, acre-feet (AF)	3180	3180
	Calculated unit O&M cost, \$/AF	\$ 84.70	\$ 85.77

* Based on Table 5-2

** Based on Table 5-3

5.1.3 Economy of Scale

There is significant economy of scale for multiple-train systems larger than 2000 gpm. Regeneration and protonation tanks and pumps are underutilized in single-train (one, 2000-gpm IX system) or dual-train (two, 1000-gpm IX systems) treatment processes. Since regeneration and protonation can be accomplished in two days or less, the duty cycle for this equipment may be less than 10% for a single train or 20% for a dual train. Therefore, the regeneration equipment for a 2000-gpm system could support the regeneration requirement for a 10,000-gpm treatment facility with little additional cost. A similar underutilization situation exists with the scavenger-resin treatment equipment. The equipment used for the 2000 gpm scenario would be adequate for a 10,000-gpm treatment system.

The pretreatment and post treatment operation would be performed in single pretreatment and post treatment systems regardless of the scale of the treatment operation. Pre- and post treatment equipment costs would be scaled proportional to the treatment requirement and the scaling exponent would be 0.5 or less.

The cost of the biodegradation system for remediation applications is not proportional to scale at the very small treatment volume required. The scaling exponent for the biodegradation system in the treatment range of 2 to 10 is less than 0.25. Therefore, a 10-gpm treatment system will cost less than 50% more than a 2-gpm treatment system.

The labor requirement for biodegradation is independent of scale for this application. Labor associated with the ion exchange process will increase modestly due to the additional regeneration events necessary for a multiple-train treatment system. Based on these economies of scale, the projected cost for a 10,000-gpm treatment system was developed and provided in Table 5-5. Operating costs are 10 to 20% lower for the 10,000-gpm system.

Table 5-5. Capital and Operating Costs for a 10,000 gpm Treatment System

	Remediation	Drinking water
Capital Cost	\$9.65M	\$9.00M
Normalized Operating Cost – per acre-foot	\$69.54	\$78.46

5.2 Cost Analysis

5.2.1 Major Cost Drivers

5.2.1.1 Groundwater Alkalinity

The amount of acid required for groundwater pretreatment to attain the pH necessary for good performance is directly proportional to groundwater alkalinity. Acid cost is \$1.03/acre-foot for every 10 mg/L of bicarbonate alkalinity in the groundwater based on sulfuric acid at \$0.05 per pound, delivered. In high pH water (>8), carbonate and hydroxide also contribute to the acid requirement. In this situation, converting total alkalinity to bicarbonate alkalinity permits accurate pretreatment costs to be developed.

5.2.1.2 Perchlorate Concentration

Groundwater perchlorate concentration directly affects the cost of scavenger resin for drinking water applications and the cost of biodegradation for high-concentration, remediation applications. Since perchlorate is very concentrated in spent regenerating solution, over 100 times more perchlorate can be exchanged onto a strong-base scavenger resin than is removed by the weak base primary resin for drinking water applications where the groundwater is less than 100 ppb. Based on a loading ratio of 100:1 (SBA equivalents for spent regenerant water to WBA equivalents for G/W), and resin replacement and disposal cost of \$180/ft³, the scavenger cost is \$1.08/acre-foot for every 10 ppb of perchlorate removed from the groundwater.

For remediation applications (>1 ppm), perchlorate biodegradation O&M cost is approximately \$2 per kg of perchlorate biodegraded. Therefore, the cost for biodegrading spent regenerating solution is \$2.47/acre-foot of groundwater treated for every 1 ppm of perchlorate removed for the groundwater.

5.2.1.3 Treated Water Alkalinity

Post treatment cost is directly proportional to the alkalinity required in the treated water. For drinking water applications, the treated water must possess properties that do not contribute to either scaling or corrosion in water distributions systems. Water alkalinity between 30 and 60 mg/L will generally satisfy this requirement. However, scaling indices, such as the Langelier Saturation Index (LSI) that are used to predict scaling and corrosion tendencies, are a function of pH, temperature, calcium hardness, total dissolved solids, and alkalinity. Therefore, specific post treatment approaches are highly dependent on site-specific water quality. For instance, a very hard water or high TDS water may not require a high residual alkalinity (<30 mg/L), and the converse may be true for soft water. Water quality will also affect treatment chemicals. Calcite (CaCO₃) is a very effective, low-cost approach to neutralize acid and increase alkalinity and hardness of low-hardness, low TDS groundwater. However, soda ash (Na₂CO₃) or caustic soda (NaOH) would be more appropriate treatment chemicals for high TDS, high alkalinity water. The conservative approach taken for this analysis uses caustic soda (\$0.15/lb. delivered). Post treatment cost is \$5.38/acre-foot for every 10 ppm of residual bicarbonate required. Alternative treatment approaches (CaCO₃, and Na₂CO₃) must be considered on a case-by-case basis and have the potential to reduce treatment cost. For a remediation application where water is re-injected into the contaminated aquifer, CO₂ removal by stripping and/or neutralization/alkalinity adjustment may not be required.

5.2.1.4 Resin Regeneration Cost

Regeneration cost is independent of groundwater perchlorate concentration below 100 ppb because the perchlorate isotherm for the resin tested is linear from 1 to 100 ppb. This means that within this linear range, the slope of the line or capacity of the resin is approximately the same. Regeneration costs are minimal for several reasons: 1) low regeneration frequency (~4 weeks), 2) near stoichiometric amounts (5% excess) of caustic needed for regeneration, and 3) near stoichiometric amounts (~5% excess) of acid needed for protonation. Remediation of water with much higher perchlorate

concentrations will result in more frequent regenerations but this is not a linear relationship. For remediation of water at Redstone Arsenal (1.5-2.0 ppm perchlorate), the regeneration frequency was modeled to be every 11 days versus every 27 days for drinking water applications (50 ppb) at a treatment rate of 3 gpm/ft³.

5.2.1.5 WBA Resin Cost

Resin replacement cost is a major component of operating cost for several reasons. The best performing commercial resin produced by Purolite cost \$500 per cubic foot. While this resin is commercially produced, production rates are relatively low at this time. Higher production rates may lead to reduced cost. Perchlorate treatment systems for drinking water require a “multi-barrier” or two-stage, lead-lag treatment configuration. This configuration, in effect, doubles the amount of resin necessary for a treatment process. Assuming that resin performance will diminish gradually over time, a 10% margin was included by increasing resin volume by 10%. The annualized cost of resin replacement was based on a 7-year life for both drinking water and remediation applications.

Table 5-6 summarizes the major operating cost components (chemicals, resin, labor, and electricity) and shows each cost component as a percentage of the total. It is evident that resin replacement cost is the primary component of O&M cost followed by pretreatment and post treatment cost for drinking water applications. Labor cost for the remediation scenario includes labor for operation of the biodegradation treatment system. Labor cost, as a percent of the total, will decrease with scale.

Table 5-6. Summary of Operating Cost Components

Cost Element	Remediation		Drinking Water	
	\$/AF	%	\$/AF	%
Pretreatment Acid	\$ 15.35	18.1%	\$ 15.35	17.9%
Post Treatment Caustic	\$ 2.69	3.2%	\$ 16.13	18.8%
Regeneration Caustic & Acid	\$ 7.34	8.7%	\$ 3.07	3.6%
WBA Resin Replacement	\$ 32.94	38.9%	\$ 32.94	38.4%
Scavenger Resin Replacement			\$ 5.41	6.3%
Effluent Biodegradation	\$ 3.70	4.4%		
Labor	\$ 19.62	23.2%	\$ 9.81	11.4%
Electricity	\$ 3.06	3.6%	\$ 3.06	3.6%
Total:	\$ 84.70	100.0%	\$ 85.77	100.0%

5.3 Cost Comparison

Treatment costs in dollars per acre-foot (\$/AF) were evaluated for five different scenarios: 1) a WBA resin application for drinking water that uses a scavenger resin to treat spent regenerating solution, 2) a WBA resin application for remediation of groundwater that uses biodegradation to

treat spent regenerating solution, 3) the strong base anion (SBA) regenerable resin process (ISEP) using CalRes 2000 that is in operation at La Puente, CA, 4) the single-use, SBA resin process using PWA2 resin that is in operation at the Lincoln Avenue Water Company site, Altadena, CA, and 5) a proposed single-use, SBA resin process using CalRes 2100 or USF 9710 planned for Castaic Lake Water Agency, CA. The cost analysis is summarized in Table 5-7.

Table 5-7. Cost Comparison Summary

System:	WBA Drinking Water	WBA G/W Remediation	SBA-ISEP La Puente	SBA Lincoln Ave.	SBA Castaic Lake
Capacity, gpm	2000	2000	2500	2000	2400
Treatment vol, AF/yr	3182	3182	3978	3182	3818
Annual O&M Cost	\$ 273,000	\$ 270,000	\$ 1,950,000	\$ 1,084,124	\$ 940,000
Capital Cost	\$ 2,615,500	\$ 2,958,000	\$ 4,800,000	\$ 2,480,000	\$ 3,700,000
Interest Rate	6%	6%	6%	6%	6%
Plant Life	20	20	20	20	20
O&M Present Worth	\$ 3,131,288	\$ 3,096,879	\$ 22,366,346	\$ 12,434,817	\$ 10,781,726
Total Present Worth	\$ 5,746,788	\$ 6,054,879	\$ 27,166,346	\$ 14,914,817	\$ 14,481,726
Treatment Cost, \$/AF	\$ 90	\$ 95	\$ 341	\$ 234	\$ 190

Costs for the WBA scenarios are based on the data provided in Table 5-4. Costs for the other scenarios were provided in a table published by the California DHS dated October 14, 2004, and based on NASA Action Memorandums dated August 24, 2004, and April 19, 2006. The actual costs provided in the DHS table for the ISEP process were \$2.8M for capital and 1.6M for O&M. However, these costs did not include treatment or disposal of the perchlorate-contaminated spent regeneration brine solution. ARA recently did an analyses under contract to the Baldwin Park Operable Unit (BPOU – controlling authority for La Puente) for brine treatment. The least expensive approach, biodegradation, would add \$2M in capital cost and \$350K in O&M cost. These costs were added to the values provided by DHS and the sum used in Table 5-7. The Lincoln Avenue system is leased. An approximate estimate of capital cost was derived by multiplying the lease cost (\$9500/mo.) by the term (20 years) and adding known site improvement costs (\$200K). The Castaic Lake system is proposed. No attempt was made to adjust the 2004 costs to 2006 values.

A 20-year plant life and 6% interest rate were used to determine the net present value of the operating costs. The results of this analysis clearly show that the water treatment cost for the WBA technology are less than 25% of current regenerable resin systems (ISEP) and less than

50% of the least expensive single-use resin systems. It is important to note that the treatment cost for the WBA technology is only slightly dependent on capital cost. This due to the large difference in operating cost of the WBA technology compared to current technologies. For instance, a 50% increase in the estimated capital cost for a WBA drinking water system from \$2.616M to \$3.923M would only increase the treatment cost from \$90/AF to \$111/AF. This is still less than one third of the cost for current regenerable resin processes and less than half the cost for existing single-use resin processes.

6. Implementation Issues

6.1 Environmental Checklist

Candidate extraction wells for this demonstration were installed in 1995 to treat groundwater for TCE removal. A NPDES permit was acquired to discharge the treated effluent to wetlands that surround the site. This activity was suspended in part due to perchlorate contamination. RSA personnel treated the perchlorate-free effluent from this demonstration and were able to discharge the treated water, after verifying that all discharge requirements were met by laboratory analysis.

Hazardous waste, including xylene and acetone, generated by the perchlorate field monitor was collected and stored until the conclusion of the demonstration. Less than five gallons of waste was generated during the demonstration. ARA coordinated the disposal of this waste with a hazardous waste disposal facility.

6.2 Other Regulatory Issues

While attending the 2005 Partners Symposium, ARA met with a CA DHS regional representative who expressed interest in this technology being demonstrated for drinking water applications. ARA has submitted a proposal to ESTCP that includes a demonstration of this technology for a drinking water application in California. One of the goals of the proposed demonstration is to collaborate with CA DHS to determine a sampling and analysis plan that will allow DHS approval of the technology.

ARA briefed this technology and the demonstration at Redstone Arsenal to water purveyors and other organizations in California in mid-December. ARA will brief the final results to Redstone Arsenal Environmental Restoration Office at their convenience. The demonstration results will also be briefed in a Groundwater Resources Association of California Conference highlighting perchlorate issues in January 2007.

6.3 End-User Issues

End-users for this technology include DOD facilities, formally used defense sites, and municipal drinking water systems that have been contaminated with perchlorate by past DOD operations. In addition to drinking water applications, the technology can be used by the DOD for pump-and-treat perchlorate remediation and to facilitate remediation of co-contaminants (such as VOCs) by enabling the removal of perchlorate before discharge or re-injection. The technology can also be applied to the treatment of wastewater generated by munitions manufacturing or demilitarization operations.

End-user concerns will likely focus on performance, cost, user friendliness, and reliability (listed in order of importance). The demonstration directly and quantitatively addressed cost and performance by executing the process described in this demonstration plan. User friendliness and reliability was qualitatively addressed by this demonstration by documenting and reporting operational issues identified as part of the demonstration.

Implementation of this technology will be straightforward. Commercial, large-scale, ion exchange equipment for WBA resin technology exists. Pretreatment and post treatment

are simply pH control unit operations that are straightforward to design and engineer. Stripping tower design and engineering for CO₂ stripping are straightforward. Treatment and reuse of residuals by ion exchange super loading, or destruction by biodegradation, are proven technologies. All processes operate at ambient temperature and low pressure (<30 psig) and, therefore, present no unique engineering challenges.

The demonstration program was designed to address all major unit operations of this technology at the pilot-scale. Pretreatment, ion exchange, post treatment, and regeneration were conducted at the scale proposed. Post treatment was accomplished in a single tank that stripped CO₂ and added caustic as required. In a full-scale system, it would be more economical to design post treatment with a CO₂ stripping tower followed by a separate neutralization basin. In the full-scale system, alkalinity of the treated water will be maintained by controlling pH and by diverting some un-stripped product water directly to the neutralization basin. Residual treatment will be conducted at a laboratory scale on residuals collected from pilot regeneration operations. However, these residual treatment technologies have been implemented at full-scale.

A patent application was filed to protect this technology, jointly owned by ARA and Purolite and efforts to commercialization the process are underway. ARA and Purolite will market this technology to a wide range of clients. ARA has many contacts with DOD agencies addressing perchlorate concerns and DOD contractors. Purolite markets their products worldwide. Purolite provides over 70% of the resin currently being used to remove perchlorate from drinking water at approximately 20 different sites in the United States. Purolite and ARA have a very large incentive to commercialize and transfer this technology to DOD and private sector.

6.4 Lessons Learned

6.4.1 Perchlorate Monitor

The primary problems with the perchlorate monitor demonstration were mechanical and control-related failures. The concept, approach, and the chemistry of the method are valid and effective. Therefore, we should have teamed with an instrument manufacturer who could have provided off-the-shelf devices that would reliably execute the mechanical and control functions. This would have permitted the demonstration effort to focus on method performance issues (detection limits, matrix interference, etc.) instead of the mechanical performance and control issues that plagued the monitor portion of this project. The monitor portion of this effort would have had to have been funded at a level two to three times the budgeted amount to resolve both the mechanical and control issues and define the chemical performance of the method.

6.4.2 Operation and Regeneration of the WBA Resin Treatment System

There were several minor lessons learned and one significant lesson learned during the demonstration. Minor lessons learned were associated with pretreatment pH and pH control, the post-treatment approach, and the regeneration approach – once through vs. circulation or recycle. To maintain the resin in the protonated state during long operation cycles (as is the case for perchlorate treatment in groundwater), it is important

to maintain the pH of the feed water at 4.3 or less. At this pH, all of the bicarbonate ions in solution (which could neutralize protonated functional groups on the resin) have been converted to carbonic acid ions or CO₂ gas in solution. This means that all of the natural buffering in the water has been removed. Also, at this pH the hydrogen ion concentration is relatively low, therefore, addition of a small amount of acid results in a large change in the hydrogen ion concentration and pH. These two factors create an environment where the pH is difficult to control. In the pilot system, this was addressed by adjusting the pH controller constants and acid concentration to achieve effective pH control. In a full-scale system that uses a concentrated acid to reduce the groundwater pH, a well engineered injection and mixing system will be necessary to maintain adequate pretreatment pH control (± 0.5 pH units). Redundant pH monitoring, process interlocks, and/or alarms will ensure proper pH control in the pretreatment system.

The post-treatment approach employed during the pilot demonstration combined CO₂ degassing and neutralization in one tank for simplicity of operation. However, this approach does not provide the control and flexibility necessary for a full-scale treatment system. In a full-scale system, CO₂ stripping operations (membrane or stripping tower if required) and alkalinity/pH restoring operations (calcite contacting, NaOH addition, or Na₂CO₃ addition) should be performed as separate unit operations in parallel (split stream) or series configurations. This will result in minimizing the size and cost of post treatment while maximizing the flexibility and performance.

Several regeneration approaches were evaluated. As predicted, regeneration by a single-pass operation resulted in the generation of a large quantity (10 to 15 bed volumes) of spent regenerating solution and excess consumption of caustic. The circulation method resulted in minimal volume of spent regenerating solution (1 to 3 bed volumes) and near stoichiometric (5 to 10% excess) caustic consumption. Similar benefits were demonstrated during protonation operations. Regeneration and protonation by circulation and controlling the pH to prevent the process equipment from being exposed to high (>12-12.5) and low (<3-4) pH excursions, prolonged the time required for regeneration. This is a valid approach if several days are available for regeneration and protonation, and materials of construction limit the pH operating range. This may be the case in a retrofit situation. In a full-scale operation, regeneration and protonation time can be greatly shortened by adding all of the caustic or acid at once, or over a short period (<1-2 hr), to the circulating regenerating/protonating solution.

While the circulation approach drastically reduces acid and caustic consumption and the volume of spent regenerating solutions, the resulting high concentration of residual perchlorate ion requires a thorough rinse operation to eliminate perchlorate bleed from the resin during on-line operation. This was the major lesson learned during the Redstone demonstration. The first two columns used in the demonstration had been pre-loaded with perchlorate, regenerated, and a short rinse (~5BV) performed. Residual perchlorate that remained in the rinse solution on the resin was re-exchanged throughout the resin bed during protonation. This resulted in a continual bleed of perchlorate (5-10 ppb) during on-line operation. It was subsequently demonstrated that a minimum rinse of 10-15 bed volumes was necessary to reduce perchlorate in the rinse water to levels (<100

ppb) that result in no measurable perchlorate bleed during on-line operation. In a multiple vessel (lead-lag), full-scale operation, the regeneration rinse can be executed in a manner that results in no net increase in spent regenerating solution. The rinse water can be treating using a scavenger resin to remove perchlorate and permit discharge or reuse. However, the preferred approach is to recycle and treat the rinse water using the on-line WBA resin ion exchange vessel. In this approach, the initial 1 to 3 bed volumes of rise (strong rinse) is retained for use in a subsequent regeneration. This strong rinse contains most of the perchlorate residual from the spent regenerating solution. The remainder of the rinse is conducted at low flow rate (2-4 BV/hr), injected into the pretreatment system for pH reduction, treated by the on-line ion exchange vessel(s), and is produced as treated water.

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8. Points of Contact

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone/Fax/Email	Role in Project
Dr Andrea Leeson	ESTCP 901 N. Stuart Street, Suite 303 Arlington, VA 22203	703-696-2118 703-696-2114 fax andrea.leeson@osd.mil	Technical Project Manager
Mr. Bryan Harre	Navy Representative, 1100 23rd Avenue Port Hueneme, CA 93043	805-982-1795 805-982-4304 fax bryan.harre@navy.mil	DOD Representative
Mr. Edward Coppola	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax ecoppola@ara.com	Technical Manager
Ms. Andrea Davis	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax adavis@ara.com	Project Manager
Mr. Steve Baxley	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax sbaxley@ara.com	QA Manager
Mr. Robert Girvin	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax rgirvin@ara.com	QA/QC Coordinator
Mr. Phil Thorne	ARA 415 Waterman Road South Royalton, VT 05068	802-763-8348 802-763-8283 fax pthorne@ara.com	Perchlorate Monitor Lead
Mr. Wes Smith	US Army Corps, Redstone Arsenal, AL	256-876-9479 256-876-0887 fax carl.smith@redstone.army.mil	Redstone Arsenal Representative
Mr. Larry Galloway	RSA Support Contractor 500 Wynn Drive, Suite 314 Huntsville, AL 35816-3429	256-842-2850 256-722-7212 fax lgalloway@amtec-corp.com	Redstone Arsenal Representative

Appendix A

Summary of Experiments and Results
for the
ESTCP Field Demonstration
at
Redstone Arsenal – Huntsville, Alabama

January 12, 2006

ESTCP PROJECT NUMBER CU-0312
ARA PROJECT NUMBER 16623

1.0 Resin Selection

Resin selection was accomplished by screening perchlorate selective resins and regeneration techniques. Commercially available resins were screened for selectivity for perchlorate, capacity for perchlorate, and potential for regeneration. Three perchlorate-selective resins, two strong base and one weak base, were identified to demonstrate perchlorate removal from contaminated groundwater at Redstone Arsenal. These resins were selected because they are very selective for perchlorate, have a high capacity for perchlorate, are potentially regenerable, and generally meet the following selection criteria:

- 1) A novel resin, treatment process, regeneration process, or resin/regenerant reuse approach.
- 2) A pilot demonstration is technically feasible
- 3) Full-scale (1000 to 10,000 gallons per minute) implementation should be economically competitive, environmentally acceptable, and relatively safe to maintain and operate.
- 4) All unit operations of a "complete" process can be demonstrated. These may include: pre-conditioning of water or resin; resin performance (capacity/efficiency); regeneration conditions and effectiveness; and generation and disposition of spent regenerating solutions including recovery, reuse, or destruction.

Table A-1 provides a brief description of the advantages and disadvantages of the three resin candidates.

Table A-1. Resin Pros & Cons

Resin	Type	Advantages	Disadvantages
Purolite D4170	Weak base	Low cost resin: < \$200/Ft ³ Easy to regenerate w/NaOH Inexpensive to regenerate Low volume regeneration (2-4 bed volumes) Disposition of regenerant Easy to neutralize Easy to biodegrade	Groundwater pH must be controlled slightly acidic Treated water requires neutralization Reprotonation of resin is necessary after regeneration. Lower treatment capacity than strong base resins
Purolite A-530E	Strong base	Low cost resin: < \$200/ft ³ High selectivity High treatment capacity Low volume regeneration (2-4 bed volumes)	Difficult to regenerate - FeCl ₃ & HCl Regeneration Cost Dilute acid rinse required after regeneration Disposition of regenerant Difficult to reuse Difficult to neutralize Difficult to destroy
Rome & Haas PWA2	Strong base	Very high selectivity Very high treatment capacity	High cost resin: > \$400/ft ³ No known regeneration mechanism

Purolite resin D4170, the weak base anion resin, was selected for laboratory and field testing because of the potential for low operating and maintenance costs, and ease of regeneration using low-risk, dilute caustic. Actual ion exchange at functional sites on the resin surface is the rate-limiting step for weak base resins. Therefore, the actual ion exchange rate is affected by both pH and the specific flow rate of the water being treated.

2.0 Laboratory Experiments

The objectives of laboratory experiments conducted are summarized in Table A-2. Detailed descriptions and results of each experiment are summarized below.

Table A-2. Laboratory Experiments

Experiment	Type (Batch or Flow)	Objective(s)	Runs	Comments
Titration	Batch	<ul style="list-style-type: none"> Determine effects of pH on exchange capacity of the resin 	1	8 titration end-points
Isotherm	Batch	<ul style="list-style-type: none"> Determine perchlorate sorption in a matrix similar to groundwater at demonstration site Use results to predict perchlorate breakthrough based on concentration in influent 	4	7-9 data points per isotherm
Column	Flow	<ul style="list-style-type: none"> Determine resin treatment capacity Demonstrate repeated loading and regeneration cycles Attain accurate material balance data 	8	4 accelerated loading (450-5,000 BVs) 4 breakthrough (10,000 BVs)

2.1 Titration

A titration of D4170 was conducted to better understand the effect of pH on the exchange capacity of the resin. The total ion capacity of D4170 is 1.1 equivalents per liter. To titrate the resin, it was first put in the basic or unionized form by adding excess 3.5% sodium hydroxide and allowing the resin to equilibrate overnight. Ten beakers were prepared by adding five milliliter aliquots of unionized resin to each beaker and labeling them according to how much acid would be added. To each beaker, increasing milliequivalents of acid was added (i.e. 10% would indicate that 110 milliequivalents of acid was added to the beaker and so on) and the pH of these samples was recorded each day until equilibrium was reached (indicated by a constant pH). The resulting plot,

shown in Figure A-1, provides an indication of resin capacity as a function of pH and the time required to achieve equilibrium.

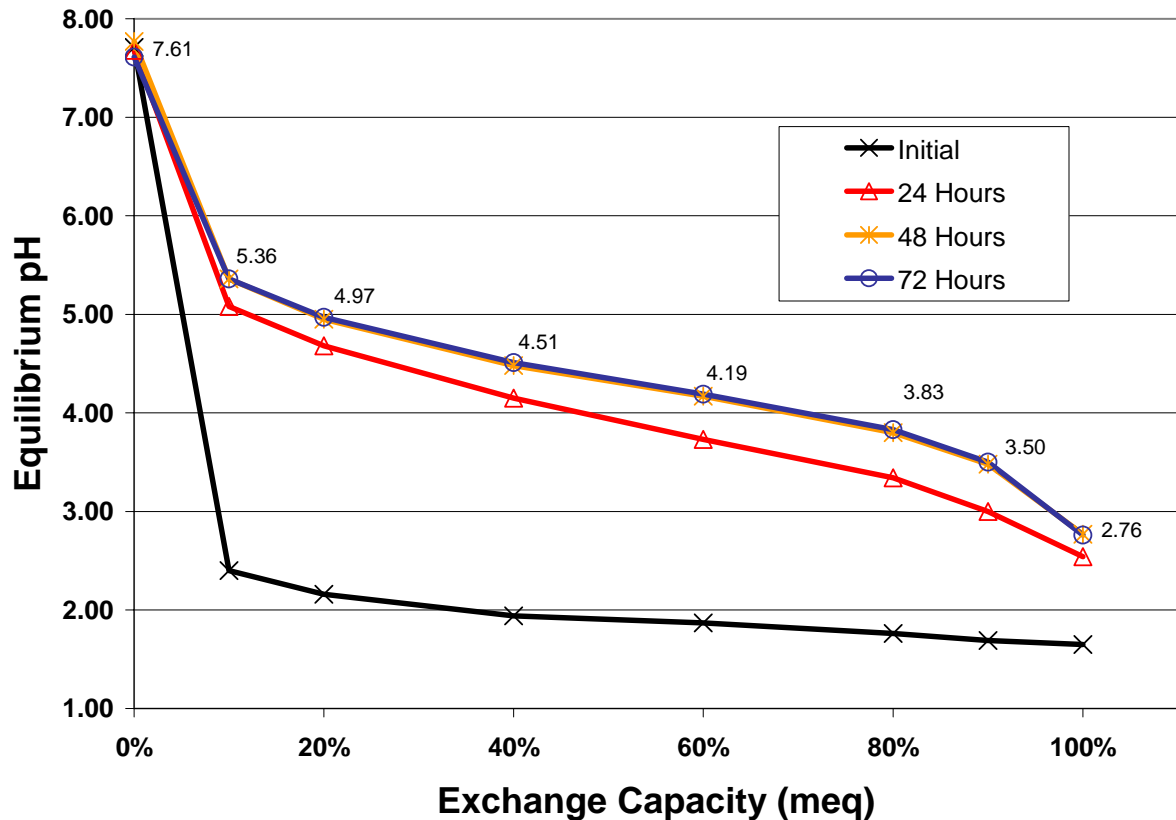


Figure A-1. D4170 Titration

2.2 Isotherm

A sorption isotherm is the concentration of a sorbed species in an ion exchange resin expressed as a function of its concentration in the external solution, in equilibrium and under specified conditions. A series of tests were initiated to determine the perchlorate sorption isotherm in a matrix similar to groundwater at the demonstration site (Redstone Arsenal). The anion concentrations of the matrix prepared for the tests are listed in Table A-3.

Table A-3. Anion Concentrations of Isotherm Matrices

Anion	Concentration (mg/L)
Sulfate	200
Nitrate	25
Chloride	35

To initiate the tests, 10 milliliters of pretreated resin (protonated and preloaded with matrix anions) was added to three flasks containing one liter of the matrix solution that

was already adjusted to pH 3, 4, and 5, respectively. Each flask was spiked with 0.10 milliequivalents of perchlorate. After equilibrium was achieved at each pH, (determined by unchanging perchlorate concentration in the solution), perchlorate was added to each flask in 0.10 milliequivalent aliquots. Figure A-2 shows the results of the sorption isotherm tests at pH of 3, 4, and 5. Based on these results as well as titration data, pH 4 was selected as the control pH for the groundwater at the demonstration.

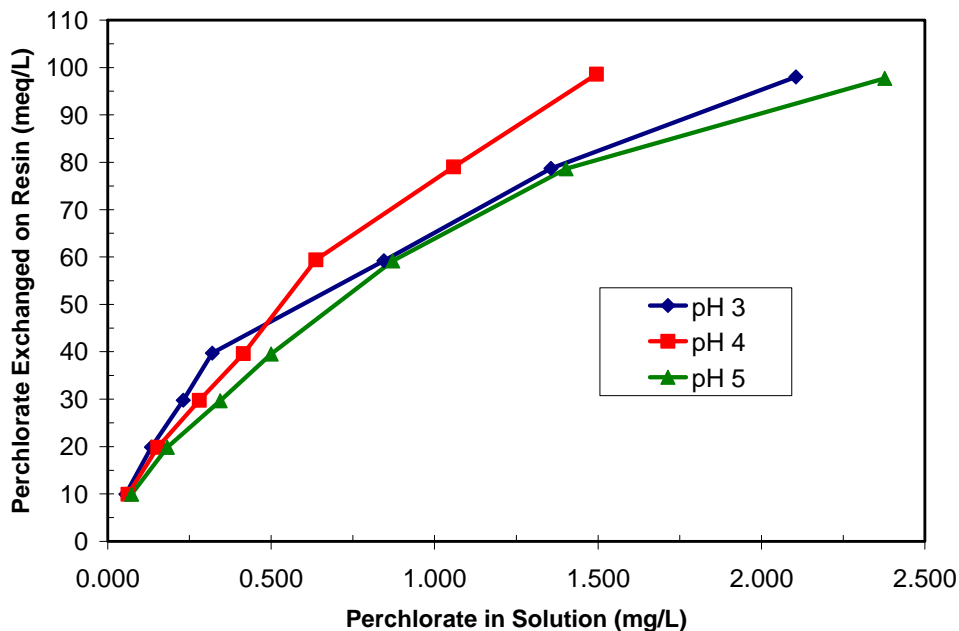


Figure A-2. Perchlorate Sorption Isotherm for D4170 at pH 3, 4, & 5

The isotherm data generated at pH 4 can be used to predict perchlorate loading concentrations and breakthrough times based on the perchlorate concentration in the groundwater. Figure A-3 shows the curve and equation used to determine the amount for perchlorate loaded on the resin. Two examples are included in the curve: groundwater concentration of 980 $\mu\text{g/L}$ (concentration in well from November 2004) and groundwater concentration of 1450 $\mu\text{g/L}$ (concentration of the surrogate water prepared for column test). Based upon predicted loading concentrations, the volume of water treated before breakthrough and the time this may occur can be predicted.

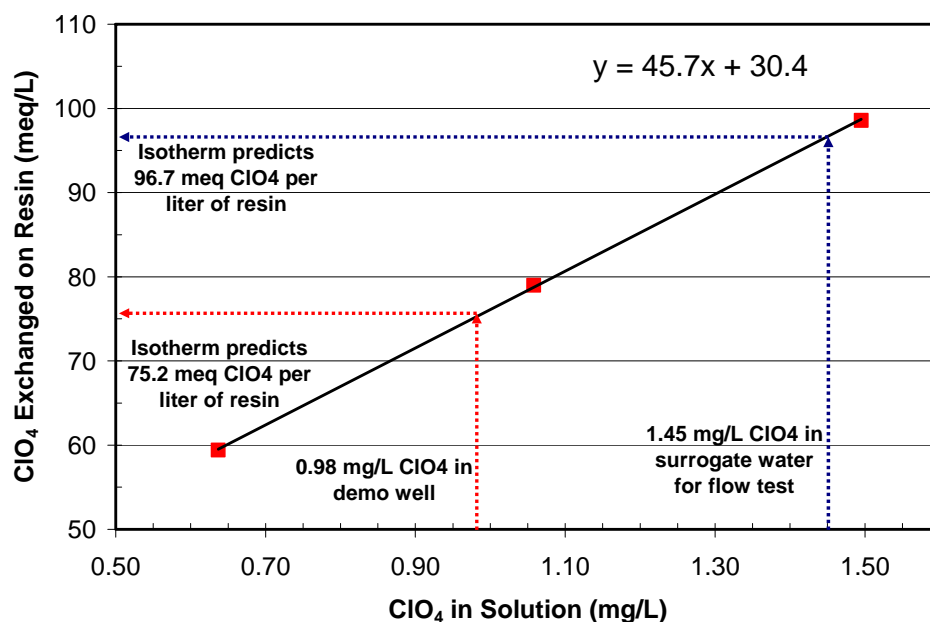


Figure A-3. Isotherm Curve at pH 4

2.3 Column Tests.

2.3.1 Accelerated Loading

The objectives of these tests were to determine the resin treatment capacity, demonstrate repeated loading and regeneration cycles, and provide accurate material balance data. Challenged water was formulated and prepared so that accelerated loading tests could be conducted. Competing anion (nitrate, sulfate, and chloride) concentration in the challenged water was adjusted to be roughly proportional to the projected anions exchange characteristics of the resin at equilibrium. The challenged water contained over 110% of the theoretical amount of perchlorate to ensure saturation. A schematic of the test setup and test sequence is shown in Figure A-4. Four test cycles were completed. The pH of the challenged water during the first three cycle tests was 5.0 and the fourth test was 6.0. The results from these tests, shown in Table A-4, indicated that this resin has high capacity for perchlorate, can be effectively and completely regenerated, and that the exchange capacity is not affected by repeated regeneration. However, during the fourth test, it was discovered that, although the pH of the challenged water feeding the resin bed was 6.0, the pH of the treated effluent did not rise above 3.8. Thus, the results did not reflect the pH 6.0 operating condition. The test method has been modified by lowering the anion concentrations in the challenged water to be representative of groundwater from Redstone Arsenal. This will result in treating more water per cycle and provide more time for treated water to achieve the desired equilibrium pH in the resin bed.

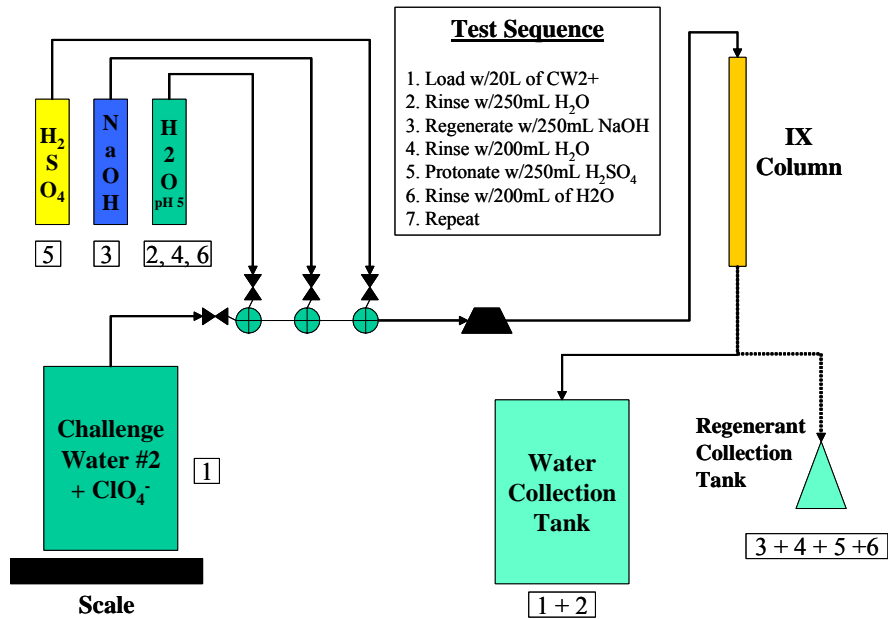


Figure A-4. Cycle Test Design and Sequence

Table A-4. Cycle Test Results

Cycle	Perchlorate Loaded (meq/liter)	Perchlorate Recovered
1	36.37	97.08%
2	37.32	99.91%
3	39.66	99.28%
4	39.23	106.25%

2.3.2 Groundwater Surrogate Loading/Breakthrough Tests

Three perchlorate loading/breakthrough tests of D4170 resin were conducted using a water surrogate simulating predicted anion concentrations of groundwater. Table A-5 lists the major anion concentrations of this simulated groundwater.

Table A-5. Anion Concentrations of Breakthrough/Loading Tests

Anion	Concentration (mg/L)
Perchlorate	0.050
Sulfate	200-300
Nitrate	25
Chloride	35

To conduct the loading/breakthrough tests of D4170, twenty inches of resin was loaded into two 3/5 inch diameter columns, resulting in a 90 milliliter resin bed volume for each column. Key parameters varied during the course of testing included pH of the challenged water; flow rate in bed volumes per hour (BV/hr); and the number of columns tested in series. Table A-6 summarizes the operational range of these key parameters established during each test. The start and end date for each test is also included.

Table A-6. Test Parameters of Column Studies

Test #	Start Date	End Date	No. of Columns in Series	CW pH	Flow Rate (BV/hr)
1	1/18/05	2/10/05	2	5.0 - 5.5	16
2	2/14/05	3/10/05	1	3.0 - 4.5	16 - 24
3	3/12/05	4/13/05	2	2.7 - 3.0	24

Table A-7 summarizes breakthrough results for each individual column during each test. Columns identified as "A" represent the lead column, and columns identified as "B" represent the lag column. The second test was conducted with only a single column. For each column, the table identifies the total volume of water treated (in bed volumes), the volume of water treated when perchlorate breakthrough occurred, and the maximum perchlorate breakthrough reached as a percentage of perchlorate concentration in the feed water.

Table A-7. Summary of Column Test Results

Test #	Column I.D.	Bed Volumes (BV) Treated	Perchlorate Breakthrough Occurrence (BV)	Max. Perchlorate Breakthrough (%)
1	A	8880	3580	75
1	B	8880	No Breakthrough	0
2	n/a	10750	3880	42
3	A	16500	4462	57
3	B	10300	9816	14

These tests were helpful in characterizing how pH and flow rate affect perchlorate breakthrough. Important information gathered from these tests include the following 1) changing pH during a test seems to change ion exchange dynamics creating unpredictable results and should be avoided, 2) for the same reasons, flow rate

changes during a test should also be avoided, 3) these tests, along with titration and isotherm tests, suggest that the best operational pH is 4, and 4) these tests confirmed that without backpressure, dissolved CO₂ will degas and create air pockets in the resin bed.

After anion concentrations were identified in the selected well (RS498), a fourth perchlorate loading/breakthrough test was conducted. A water surrogate was prepared to simulate groundwater at the site. The anion concentrations of the prepared water are listed in Table A-8. The pH of this water was controlled at 3.8 using sulfuric acid.

Table A-8. Anion Concentrations of Breakthrough/Loading Test 4

Anion	Concentration (mg/L)
Perchlorate	1.45
Sulfate	220
Nitrate	<1
Chloride	22

Two 3/5-inch diameter columns were prepared by loading approximately twenty inches of resin into each column. During the previous three tests, flow rates and calculations were based on each column, identified as either lead or lag. The flow rates and calculations during this fourth test were based on two columns representing a single, 40-inch column. So effluent from the first column was considered the “mid-point” and effluent from the second column was the treated water. This was done to better simulate the larger bed-depth columns that will be used in the demonstration. The flow rate, based on the combined bed depth of the two columns, was 13 bed volumes per hour. Figure A-5 is a plot of perchlorate breakthrough of the mid-point and the final treated water.

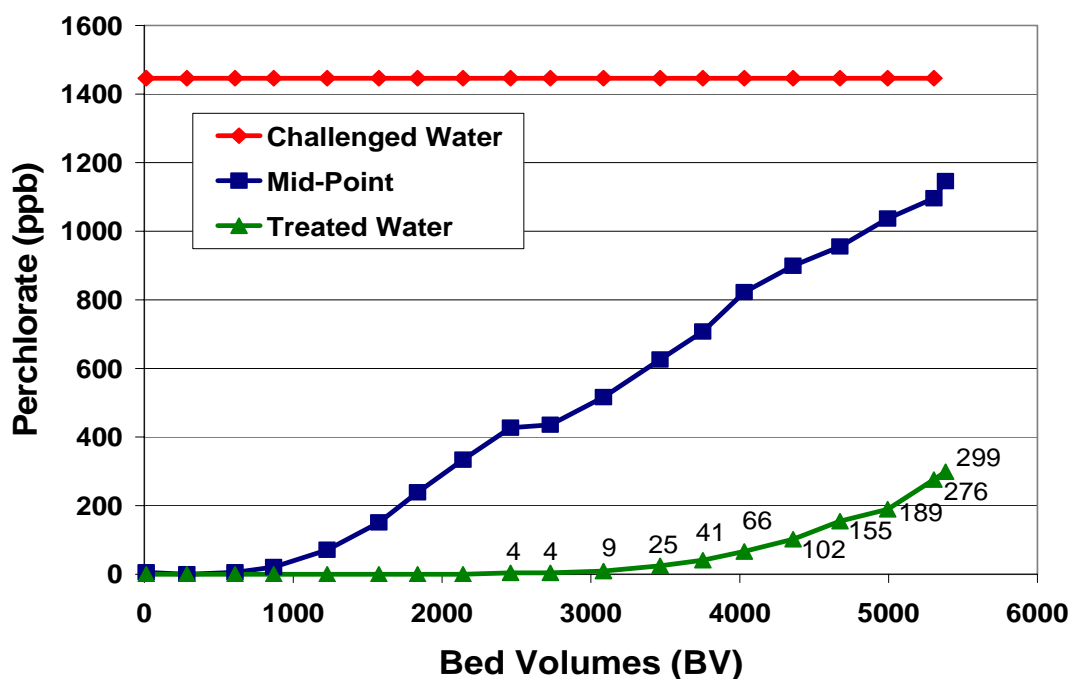


Figure A-5. Perchlorate Breakthrough in Test 4

3.0 Field Experiments

Three columns, identified as C1, C2, and C4, were used throughout the demonstration. Each column had an internal diameter of 2.049-inches and was packed with 36-inches of Purolite D4170 resin. The resin bed volume was calculated to be 1.945 liters. Prior to initiating the demonstration, each column was preconditioned to minimize any uncharacteristic behavior that may result from using virgin resin. Preconditioning consisted of protonating, loading with perchlorate using a surrogate water, regenerating, and protonating in preparation for treating groundwater at the demonstration site.

There were five test periods during the demonstration at Redstone Arsenal. Key operating parameters for each test period, including flow rate, column identification for the lead and lag positions, and the post treatment conditions, are provided in Table A-9.

Table A-9. Operating Conditions during each Test Period

Test Period	Flow Rate (BV/hour)	Flow Rate (GPM)	Lead Column ID	Lag Column ID	Caustic Conditions
1	12	0.10	C1	C2	Set point at 6.8; air pump controlled with caustic addition.
2	12	0.10	C2	C4	Set point at 7.4; air pump on continuously.
3	12	0.10	C4	C1	Set point at 7.4; air pump on continuously.
4	18	0.15	C1	C2	Set point at 6.8; air pump on continuously.
5	24	0.21	C2	C4	Set point at 6.8; air pump on continuously.

For each test period, two columns were positioned in series, in a lead-lag configuration. At the end of each test period, the column in the lag position replaced the column in the lead position, and a regenerated column was placed in the lag position. The lead column removed from service was regenerated in ARA's laboratory in Panama City, FL. During the demonstration, columns 1 and 2 were regenerated three times (including pre-conditioning) and column 4 was regenerated twice. All columns were reused during two test periods as shown in Table A-9.

3.1 Data Summary from each Test Period

Perchlorate results using EPA Method 314.0 from the five test periods are summarized in Figures A-6 through A-10. Each figure shows perchlorate concentrations in the feed water, and perchlorate breakthrough from the lead and lag columns. During the first test period (Figure A-6), perchlorate leakage was observed from both columns (C1 and C2). We determined that the cause of the apparent leakage was insufficient rinsing during preconditioning (described in section 3.0). The regeneration rinse procedure was modified and column 4 was regenerated using the new rinse procedure. During test period 2, no leakage was observed from C4. Also, no leakage was observed in any other test period, even when the flow rate was increased to 18 and 24 bed volumes per hour (Figures A-9 and A-10).

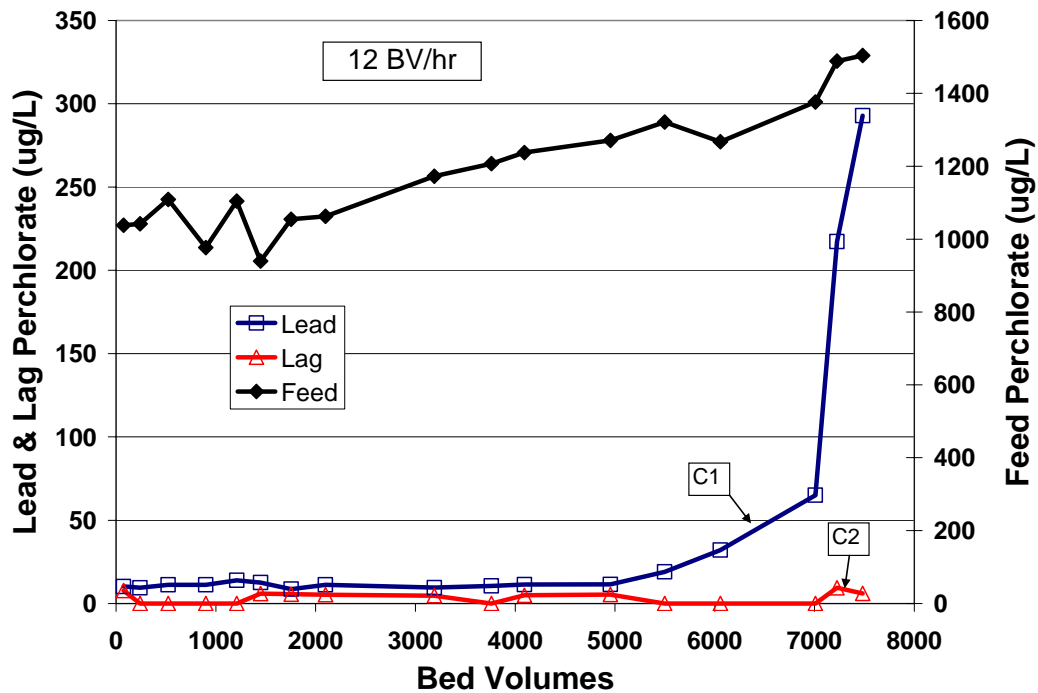


Figure A-6. Test Period 1

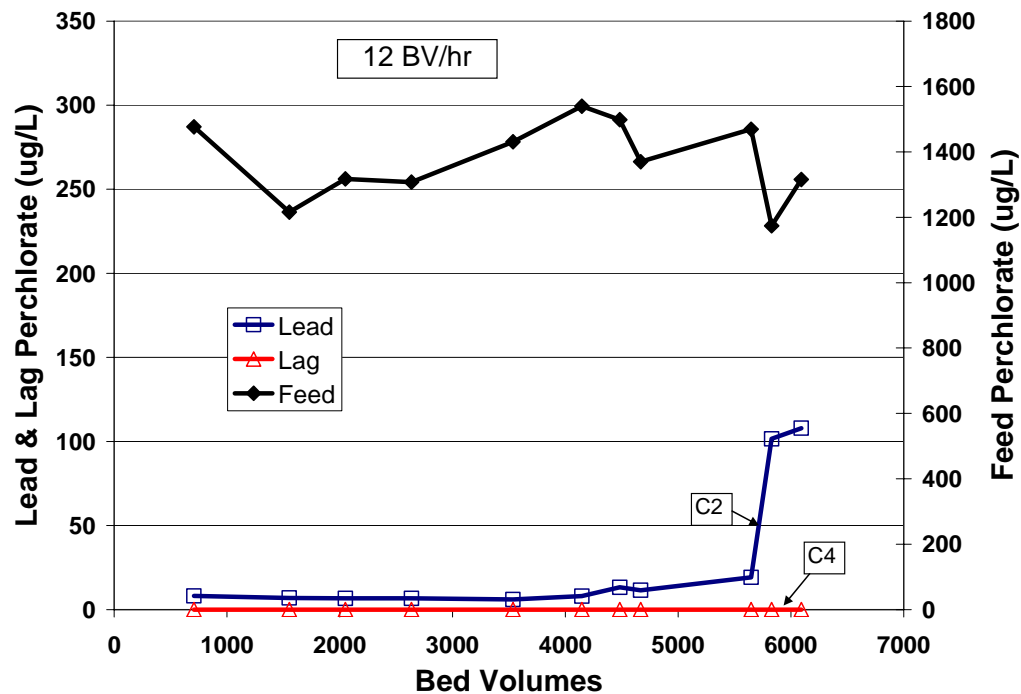


Figure A-7. Test Period 2

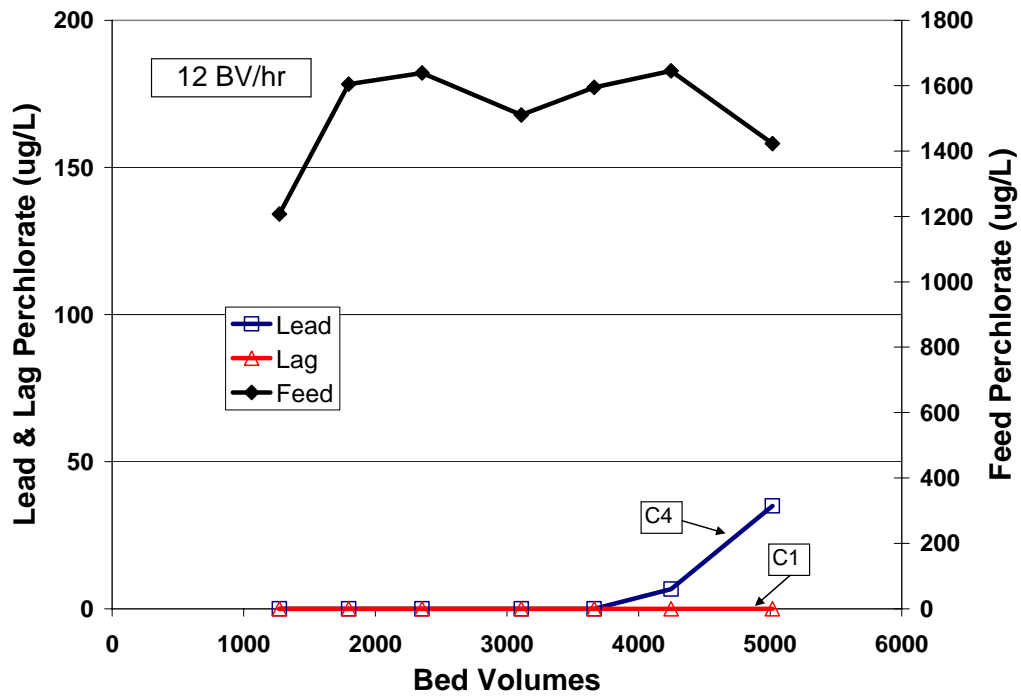


Figure A-8. Test Period 3

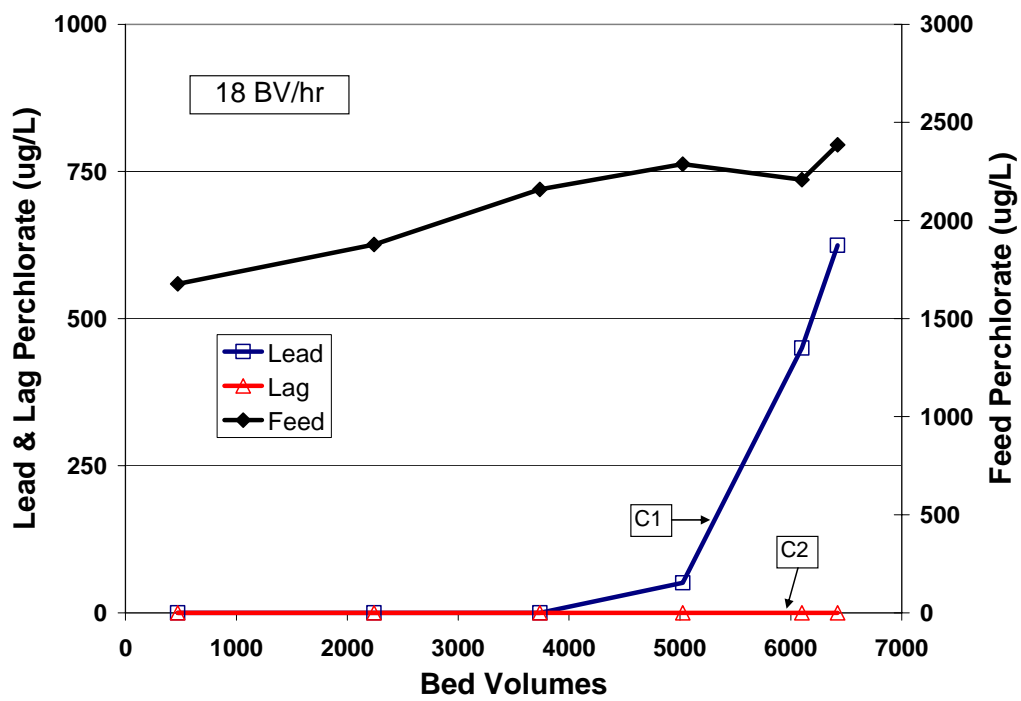


Figure A-9. Test Period 4

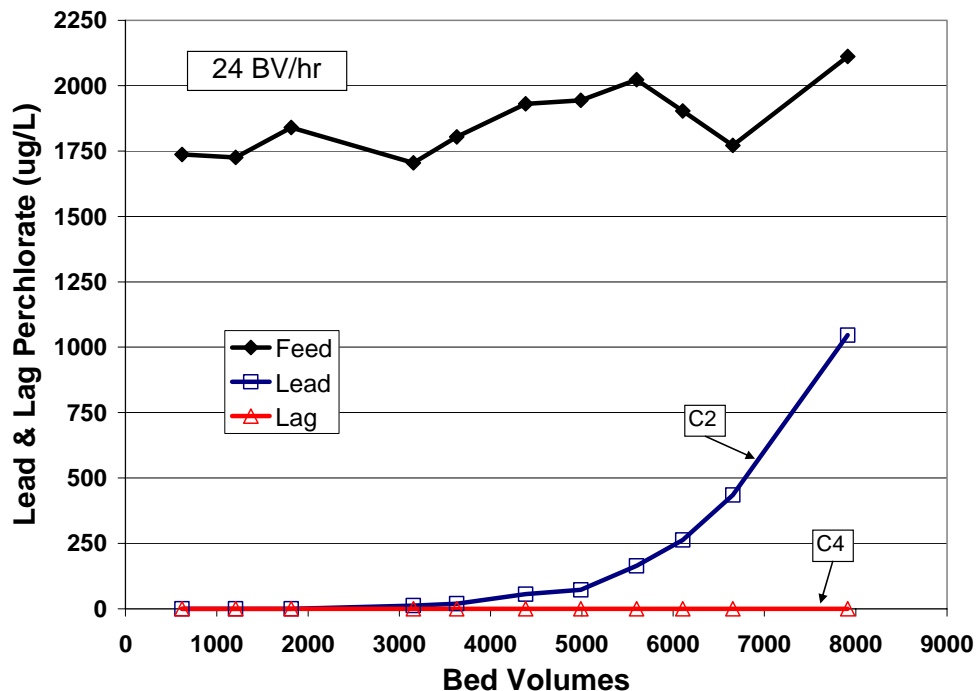


Figure A-10. Test Period 5

3.2 Test Period Interruptions

There were two occasions during the demonstration when a test period was interrupted. The first occurrence was a safety measure during landfall of Hurricane Katrina. This resulted in early termination of test period three with lower breakthrough of perchlorate than desired.

The second interruption occurred prior to start up of the fifth test period. Start up was postponed for five days because of limited treatment capacity at Redstone Arsenal's VOC treatment plant. The test period was initiated as soon as analytical results indicated that treated effluent met discharge requirements.

4.0 Regeneration and Residual Testing

4.1 Regenerating Spent Columns

Table A-10 is a summary of regeneration data. Each column is identified along with perchlorate breakthrough during the test period, the calculated amount of perchlorate loaded on the column, the amount of perchlorate contained in the regenerant, and the percent recovery of perchlorate. The percent breakthrough was calculated based on the highest concentration of perchlorate measured in the column effluent (collected on the last day of the test period) divided by the average perchlorate concentration in the influent throughout the test period. This is an approximate value because the feed concentration did vary during each period. The calculated perchlorate load for the column is an approximate value based on perchlorate concentration in the influent water, the perchlorate breakthrough concentration, and the total flow during each sampling period. Total flow was obtained using a digital flow meter. The digital flow meter was

calibrated before initiating each test period. The regenerant value reported is the amount of perchlorate in the regenerating and rinse solutions calculated from concentration and volume.

Table A-10. Regeneration Summary

Regen. #	Column ID	Break-Through* (%)	Calculated** Load (meq ClO₄)	Regenerant (meq ClO₄)	Recovery (%)	Regeneration Method
1	C1	25	177	177	100	Up flow, fluidized bed with scavenging
2	C2	8	169	145	87	Up flow, fluidized bed
3	C4	2	136	140	104	Down flow, low flow rate
4	C1	30	228	191	84	Up flow, high flow rate/short cycle
5	C2	56	266	255	96	Up flow, high flow rate/long cycle

* Approximate value calculated using highest perchlorate concentration in effluent and the average perchlorate concentration in influent during the test period.

** Approximate value based on perchlorate concentrations in the influent and column effluent and the total flow between samplings.

4.2 Perchlorate Removal/Destruction from Regenerant Solutions

4.2.1 Superloading

A superloading process was designed to demonstrate a “zero-discharge” spent regenerant treatment process. Strong base anion resin Purolite A600 was used as the scavenger resin. Spent regenerant and regenerant rinse water collected from regeneration of column 1 from test period 1 was treated according to Figure A-11.

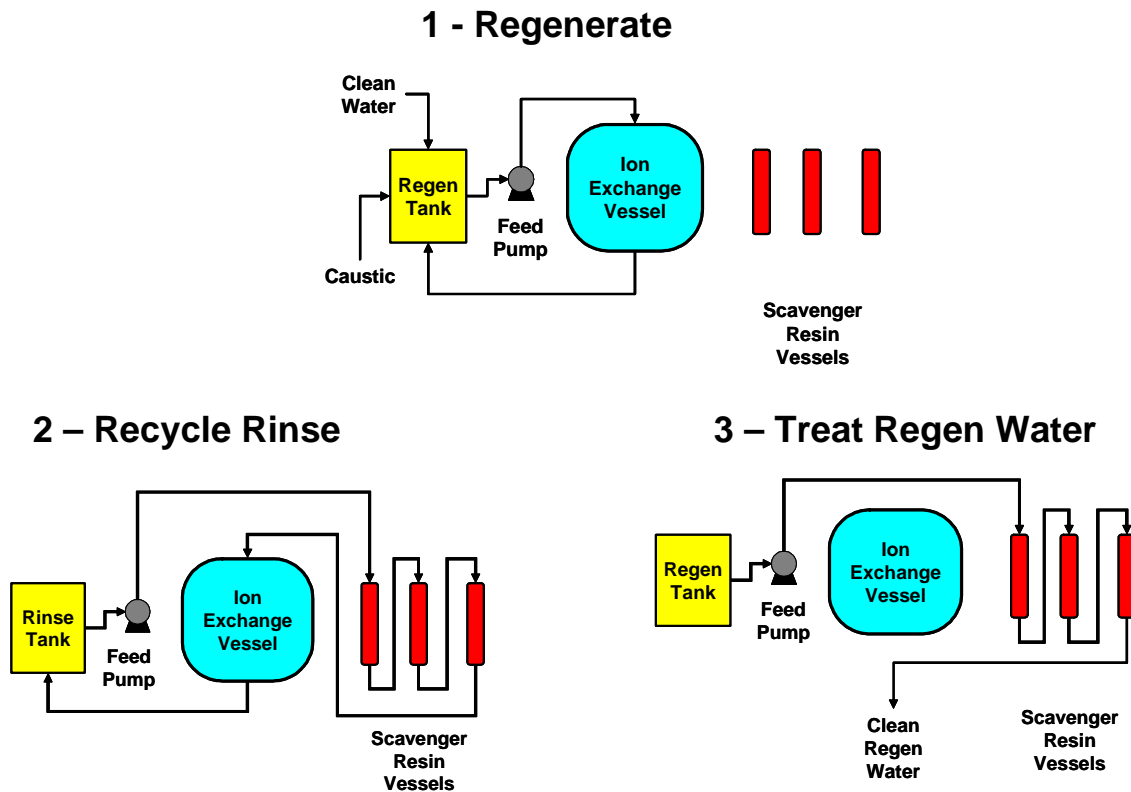


Figure A-11. Superloading Process

Perchlorate results from treating the spent regenerant are shown in Figure A-12. The starting perchlorate concentration in the spent regenerant was 1950 mg/L. The effluents from scavenger columns 1 & 2 are shown. Perchlorate concentration in scavenger column 2 effluent was never above non-detect (<4 µg/L) concentration. Scavenger column 3 effluent, which is not shown in this figure, also never exceeded 4 µg/L.

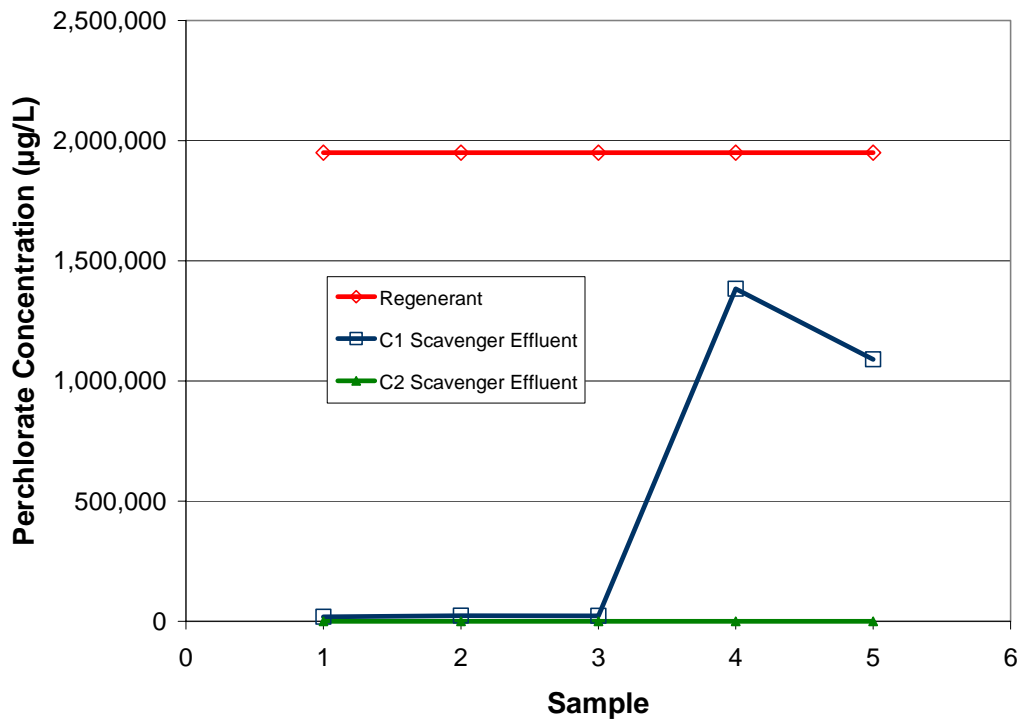


Figure A-12. Superloading Results

Scavenger studies successfully demonstrated the ability to regenerate a spent WBA column without generating a perchlorate concentrated waste stream that must be discharged.

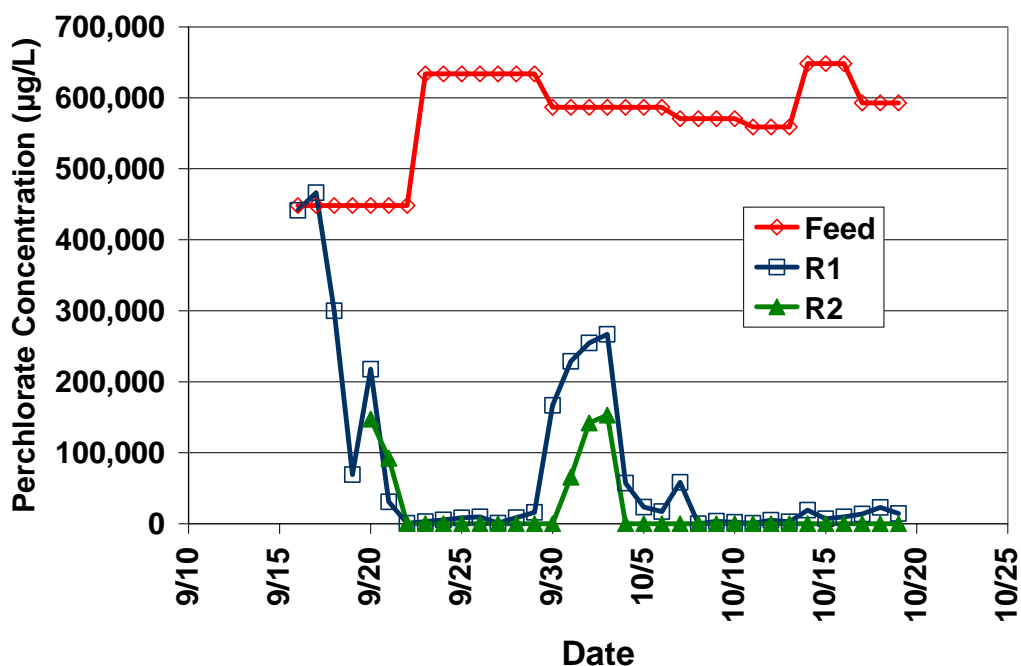
4.2.2 Spent Regenerant Biodegradation Study

Regenerant and rinse waters collected from regenerations two through four were used for biodegradation tests. The combined waters had total dissolved solid concentrations of approximately 9950 mg/L. Two 2.5-liter reactors were arranged in series and inoculated using surrogate water. After successful inoculation and start up, flow of the regenerant/rinse waters were initiated on 9/23/05 and stopped on 10/19/05, for a total of 33 days of biodegradation operation. A table of hydraulic resident times, flow rates, and nutrient concentrations are provided below (Table A-11).

Table A-11. Biodegradation Parameter Summary

Start	HRT	Nutrient	Water Feed Rates			Nutrient Feed Rates	
Date	hr	Conc. g/L	L/day	ml/hr	ml/min	ml/day	ml/hr
19-Sep	24	2.4	2.50	104.2	1.7	10.3	0.43
23-Sep	24	3.6	2.50	104.2	1.7	15.4	0.64
24-Sep	24	3	2.50	104.2	1.7	12.8	0.53
29-Sep	18	2.4	3.33	138.9	2.3	13.7	0.57
3-Oct	18	3.6	3.33	138.9	2.3	20.5	0.85
6-Oct	12	3.6	5.00	208.3	3.5	30.8	1.28
10-Oct	12	3.15	5.00	208.3	3.5	26.9	1.12
11-Oct	12	2.4	5.00	208.3	3.5	20.5	0.85
13-Oct	8	2.4	7.50	312.5	5.2	30.8	1.28

During biodegradation tests, the influent and the two reactors in series (R1 and R2) were sampled daily. Perchlorate results using EPA Method 314.0 are shown in Figure A-13. Perchlorate was rapidly reduced from the feed concentration (approximately 450-625 mg/L) to non-detect (< 4 µg/L) in R2. There was a three day period from 10/1/05 to 10/3/05 when perchlorate concentrations were above the detection limit. This corresponds to a nutrient reduction initiated on 9/29/05. Once the nutrient concentration was increased on 10/3/05, perchlorate concentrations were once again below the detection limit. Results indicate that regenerant diluted to 9950 TDS can be biodegraded easily.

**Figure A-13. Biodegradation Results**

Appendix B

Quality Assurance Project Plan for the ESTCP Field Demonstration

at

Redstone Arsenal – Huntsville, Alabama

May 25, 2005

**ESTCP PROJECT NUMBER CU-0312
ARA PROJECT NUMBER 16623**

1. Project Description and Objectives

1.1 Purpose of Study

The Environmental Science and Technology Certification Program (ESTCP) was created in order to develop, demonstrate, and establish the commercial potential of innovative technologies for treating contaminants found at United States Department of Defense (DOD) and DOD related sites across the country. Through ESTCP demonstrations, DOD acquires the performance and cost data necessary to properly consider innovative technologies in the remedial action decision-making process. Applied Research Associates, Inc (ARA) was selected to demonstrate recent technology advances in monitoring, removing and destroying perchlorate from groundwater sources.

Lab and field tests have demonstrated that perchlorate specific resins offer high selectivity and affinity for perchlorate that results in several benefits when compared to conventional ion exchange processes: (1) higher exchange capacity, (2) higher removal efficiency resulting in lower concentrations of perchlorate in the treated water, (3) higher specific water treatment capacity and rate, and (4) minimal impact to groundwater composition. Perchlorate selective as well as non-selective ion exchange resins are currently fielded for perchlorate removal from groundwater. However these current systems each have specific drawbacks restricting wide scale implementation. These liabilities include: 1) high cost of resin replacement and incineration costs for non-regenerable, perchlorate selective ion exchange systems 2) large volume of residuals generated by non perchlorate selective regenerable systems, and 3) the difficulty and high cost of treating residuals.

The technology proposed for demonstration takes advantage of the performance of a perchlorate selective resin while addressing and minimizing the liabilities found in current fielded ion exchange processes. The field monitor used during this demonstration brings the benefit of on-line perchlorate monitoring in both the groundwater and ion exchange effluents. This technology will provide near real-time data for perchlorate breakthrough from the ion exchange columns to concentrations as low as 1 ppb. Currently, the only available technology for measuring perchlorate at this concentration is with laboratory analytical techniques such as high pressure liquid ion chromatography.

1.2 Site Description

To achieve these objectives, a field demonstration evaluating this technology will be conducted at Redstone Arsenal using groundwater as the medium. Redstone Arsenal, located in Huntsville, Alabama, has existing monitoring and extraction wells with perchlorate contaminated groundwater ranging from very low parts per billion up to 10,000 ppb. Installation restoration program officials at Redstone Arsenal are assisting with site selection for the demonstration by providing ARA with water quality characteristics of the available wells.

Site OU-10 at Redstone Arsenal has approximately 400 monitoring or extraction wells with perchlorate contamination ranging from very low parts per billion up to 10,000 ppb. Many of these wells also have VOC contamination, primarily TCE, which will have to be considered prior to well selection. Redstone Arsenal has assisted with site selection for the demonstration by providing ARA with perchlorate, TCE, and pump rate data for groundwater extraction wells. Well selection guidelines also include having the minimum TCE contamination as possible while maintaining the capability to pump at a sufficient rate for the demonstration system. Existing infrastructure was also a consideration as the demonstration system requires power and communication lines.

ARA visited Redstone Arsenal on April 1, 2005 to discuss site selection and demonstration issues with Redstone Environmental personnel. During this visit a number of extraction wells were identified that meet the site selection requirements. Of the locations identified, well RS498, shown below in Figure B-1, was selected as the primary demonstration well, with RS497 and RS496 identified as secondary choices.

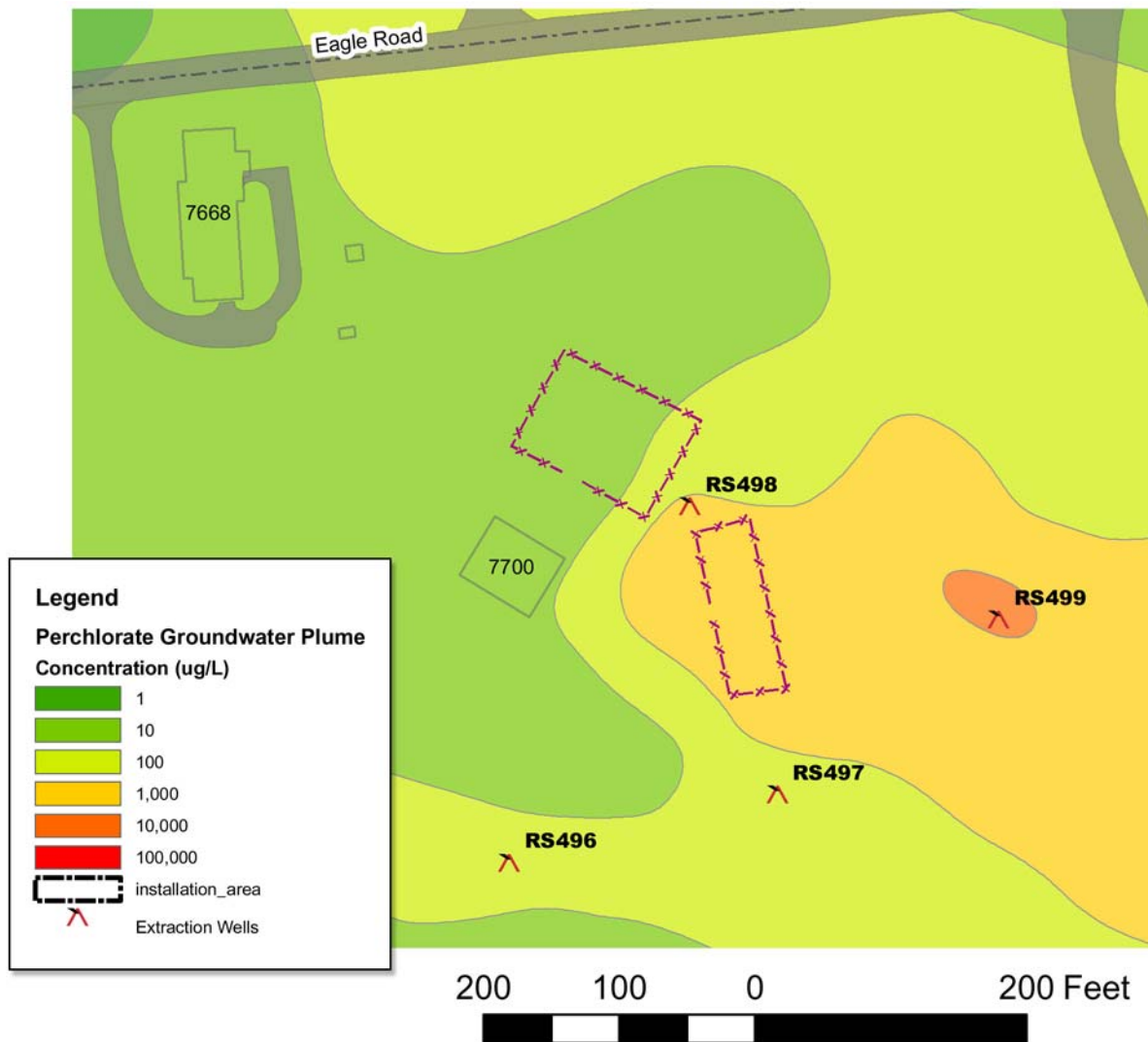


Figure B-1. Extraction Well Candidates at Redstone Arsenal

1.2.1 Operational History

Redstone Arsenal is located in the heart of the Tennessee Valley, in northern Alabama. The facility was built in 1941 to produce conventional chemical ammunition for use in World War II. For more than 40 years, Redstone has been the heart of the Army's rocket and missile programs. Dr. Werner von Braun and his German rocket experts developed the first ballistic missile; this led to the establishment of NASA's Marshall Space Flight Center in 1960. Today, Redstone is home to the U.S. Army Aviation and Missile Command (AMCOM), the Space and Missile Defense Command, numerous Program Executive Offices (PEO), and major components of the Defense Intelligence Agency and the Missile Defense Agency. Also located here are numerous tenant and satellite organizations. "Team Redstone's" mission is perform basic and advanced weapons system research and development, placing the right missile and aviation systems with the troops, keeping them ready to fight, providing weapon

systems, services and supplies to our allies, to manage weapon systems such as the Cobra and PATRIOT, and to support project managers within the program executive office structure.

Redstone Arsenal has pump-and-treat capability for removing VOCs from groundwater. However, these operations have been terminated partly due to perchlorate contamination. Currently, there are no pump-and-treat operations underway for perchlorate treatment at Redstone Arsenal. No manufacturing activities were conducted at Redstone Arsenal.

1.3 Technology Description

This demonstration will evaluate an innovative perchlorate-selective ion exchange technology for removing perchlorate from groundwater. A number of perchlorate selective resins were evaluated at the lab scale for selecting the most promising technology to demonstrate in the field. The technology selected for pilot demonstration is based on a weak base anion (WBA) exchange resin that is both perchlorate-selective and regenerable. The WBA exchange resin selected for this demonstration has high selectivity and capacity for perchlorate. However, unlike strong base anion resins, WBA resins require groundwater pretreatment to reduce pH to below the pKa value of the resin. Ion exchange behavior of all resins is primarily determined by fixed ionic functional groups attached to the resin backbone. When the pH is high, WBA resin functional groups, such as NH_3^+ , lose a proton to form the uncharged NH_2 , which is not able to attract anions from solution. Since neutralization of fixed charges increases with pH, the performance of WBA resins is pH-dependent.

The primary advantages of WBA resin technology are the ease and simplicity of regeneration, the small volume of spent regenerating solution produced, the resulting lower O&M cost of regeneration, and the lower cost and ease of disposal of spent regenerating solutions. Following regeneration of the resin with caustic, ionic groups on the WBA resin must be reprotonated using dilute acid. Effluent from reprotonation can be used to neutralize the spent caustic regenerating solution and rinse water prior to discharge or perchlorate destruction. This technology is effective for treating perchlorate contamination in any surface, ground, or drinking water application. Because of inexpensive regeneration, this technology will likely be much more economical than the single use approach, especially at higher perchlorate concentrations.

1.4 Project Objectives

This project will evaluate and demonstrate a complete ion exchange process for perchlorate removal from groundwater that includes a regenerable, perchlorate-selective ion exchange resin; a perchlorate field monitor with ppb detection; an efficient regeneration technique that greatly minimizes waste volume; and methods for treating regeneration waste.

Specific objectives are listed below:

5. Demonstrate perchlorate removal in groundwater from >50 ppb to < MCL with a regenerable, perchlorate-selective ion exchange process,

6. Demonstrate an efficient regeneration technique of the perchlorate-selective ion exchange resin. Regenerant volume should be $< 0.1\%$ of treated groundwater stream,
7. Demonstrate removal or destruction of perchlorate ($< \text{MCL}$) in the regenerant stream enabling discharge or reuse of the regenerant stream, and
8. Demonstrate the performance of a perchlorate field monitor capable of on-line, real-time perchlorate analysis with a minimum detection limit of 1 ppb.

2. Project Organization and Responsibility

This section of the QAPP addresses the project organization and division of responsibilities amongst the parties involved in this project, which is being undertaken by ESTCP. The QA/QC functions have been organized to allow independent review of project activities. The overall assignment of responsibilities are discussed below and outlined in the organizational chart included as Figure B-2.

2.1 Overall QA Management Organization

The objectives of the quality assurance and quality control (QC) efforts for this program are to assess and to document the precision, accuracy, and adequacy of the process data developed during sampling, monitoring, and analysis. The following management responsibilities have been assigned as an inherent part of this process.

ARA Program Manager (Ms. Andrea Davis): The ARA Program Manager (PM) has the final responsibility for completing this project in accordance with the Program objectives and within the schedule and budget constraints. The ARA PM also has the ultimate responsibility for the overall ARA technical effort. This includes the timely, cost-effective execution of all project activities. The ARA PM will maintain communication with all interested parties. Subcontractors will immediately report any technical problems to the ARA PM. The ARA PM will apprise the ESTCP TPM of project status and discuss project development. The ARA PM will distribute the final QAPP as approved by ESTCP to all personnel.

ARA Technical Lead (Mr. Edward Coppola): The ARA technical lead will provide technology guidance, system design and engineering, and operational support.

ARA Technical Lead (Edward Coppola): The ARA technical lead will provides technology guidance, demonstration system design and engineering, and operational support.

ARA QA Manager (Mr. Steve Baxley): The ARA QA Manager holds the overall responsibility for ESTCP QA activities. He will review the QAPP, evaluate the QC program for ARA and its subcontractors, and assure that the results of all QA/QC activities are properly incorporated, performed, and documented.

ARA QA/QC Coordinator (Mr. Robert Girvin): The ARA QA/QC Coordinator provides assistance in the generation and review of the QAPP and to ensure that data generated by subcontractors satisfies data quality and project objectives. The ARA QA/QC Coordinator reports directly to the ARA QA Manager and indirectly to the ARA PM.

Redstone Arsenal Representative (Mr. Wes Smith): The site representative is responsible for coordinating on site activities with the project contractor (ARA). The site representative will communicate site specific health and safety and environmental requirements prior to execution of the field demonstration.

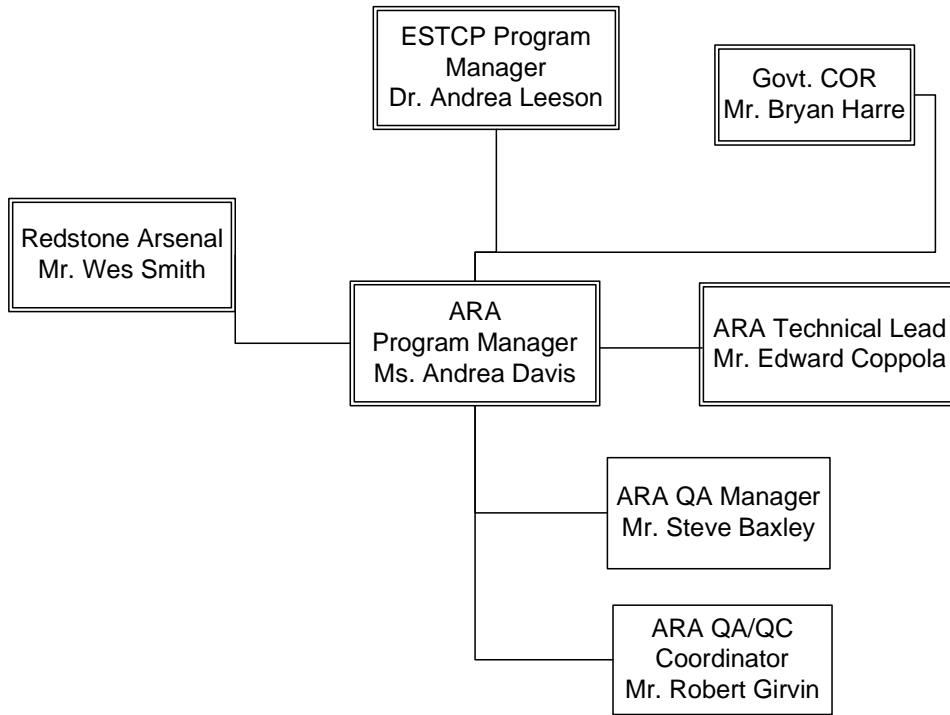


Figure B-2. Responsibility Organization Chart

2.2 Key Personnel Contact Information

POINT OF CONTACT Name	ORGANIZATION Name Address	Phone/Fax/Email	Role in Project
Dr Andrea Leeson	ESTCP 901 N. Stuart Street, Suite 303 Arlington, VA 22203	703-696-2118 703-696-2114 fax andrea.leeson@osd.mil	Technical Project Manager
Mr. Bryan Harre	Navy Representative, 1100 23rd Avenue Port Hueneme, CA 93043	805-982-1795 805-982-4304 fax bryan.harre@navy.mil	DOD Representative
Mr. Edward Coppola	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax ecoppola@ara.com	Technical Manager
Ms. Andrea Davis	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax adavis@ara.com	Project Manager
Mr. Steve Baxley	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax sbaxley@ara.com	QA Manager
Mr. Robert Girvin	ARA 430 W. 5th St, Ste 700 Panama City, FL 32401	850-914-3188 850-914-3189 fax rgirvin@ara.com	QA/QC Coordinator
Mr. Phil Thorne	ARA 415 Waterman Road South Royalton, VT 05068	802-763-8348 802-763-8283 fax pthorne@ara.com	Perchlorate Monitor Lead
Mr. Wes Smith	US Army Corps, Redstone Arsenal, AL	256-876-9479 256-876-0887 fax carl.smith@redstone.army.mil	Redstone Arsenal Representative
Mr. Larry Galloway	RSA Support Contractor 500 Wynn Drive, Suite 314 Huntsville, AL 35816-3429	256-842-2850 256-722-7212 fax lgalloway@amtec-corp.com	Redstone Arsenal Representative

3. Experimental Approach

To demonstrate this ion exchange technology using weak base anion (WBA) resin as an effective perchlorate water treatment process, a pilot system composed of three major unit operations was designed. The complete system includes units for pH pretreatment, ion exchange, and pH post-treatment.

pH Pretreatment

In order for the WBA resin to be effective, the groundwater pH must be below the pKa of the resin. It was determined in the laboratory that the capacity of the WBA resin for perchlorate increased as pH decreased. The pH range for an efficient operation was determined to be between 2.5 to 5.5. To achieve higher perchlorate capacity, the pH of the groundwater will be reduced by addition of acid in a pretreatment step prior to ion exchange (Figure B-3). To accomplish this, groundwater will be pumped from the well head to a level-controlled storage tank and then metered into a pressurized pH pretreatment system. The pH pretreatment system consists of a pH controller, an acid feed system, and a circulation pump and mixing vessel. Groundwater pH will be controlled at an optimal value of 4.0 for the duration of the field demonstration. The system is pressurized to keep carbon dioxide in solution as dissolved CO₂ and carbonic acid. The pH adjusted groundwater will pass through a micron filter to remove solids prior to entering the ion exchange unit. A pulsation dampener will minimize pressure and flow fluctuations in the ion exchange system and a flow totalizer will monitor total groundwater volume treated.

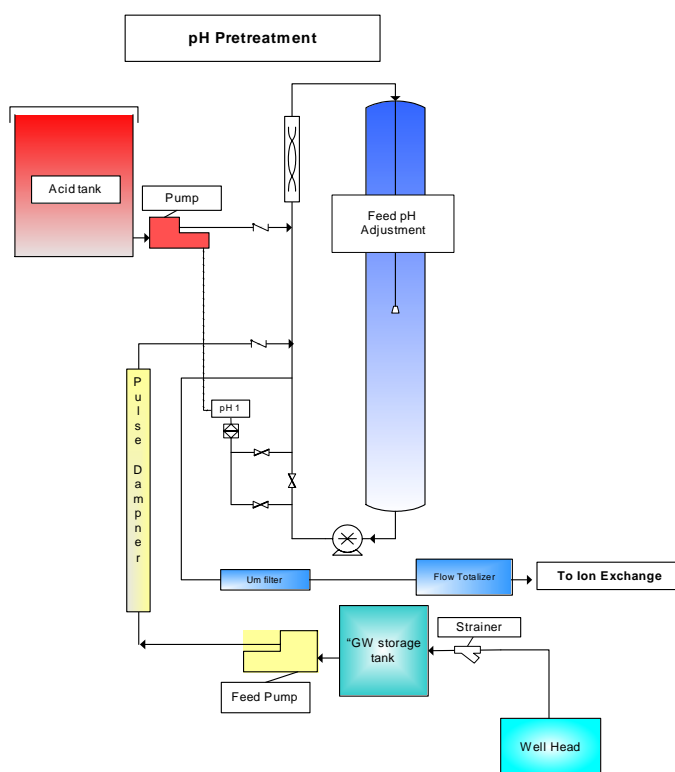


Figure B-3. Pretreatment

Ion Exchange & Field Monitor

The ion exchange unit, shown in Figure B-4, consists of two ion exchange columns in series. The pretreated water will flow through these columns in a lead-lag configuration. When perchlorate breakthrough in the lead column exceeds a predetermined value, the column will be removed from the system for regeneration, the lag column will replace the lead column, and a freshly regenerated column will be installed as the lag column. The perchlorate-loaded lead column will be shipped to ARA's Panama City, Florida laboratory for regeneration and returned to the field demonstration. This cycle will be repeated until the conclusion of the demonstration. Near real-time data provided by the perchlorate field monitor permits operation of the ion exchange system in a manner that will maximize the perchlorate loading of the lead column and, thereby, minimize the frequency of regeneration.

Three sample locations, the feed stream and discharge from each column, are configured for both automated and manual sampling. A solenoid valve controls sampling for the perchlorate field monitor. Pressure and pH are also monitored at each sample location. The perchlorate field monitor will control sampling events and data acquisition. At least one time per day, each sample location will be analyzed for perchlorate and the pressure and pH will be recorded. A back pressure regulator will maintain system pressure to prevent carbon dioxide gas formation.

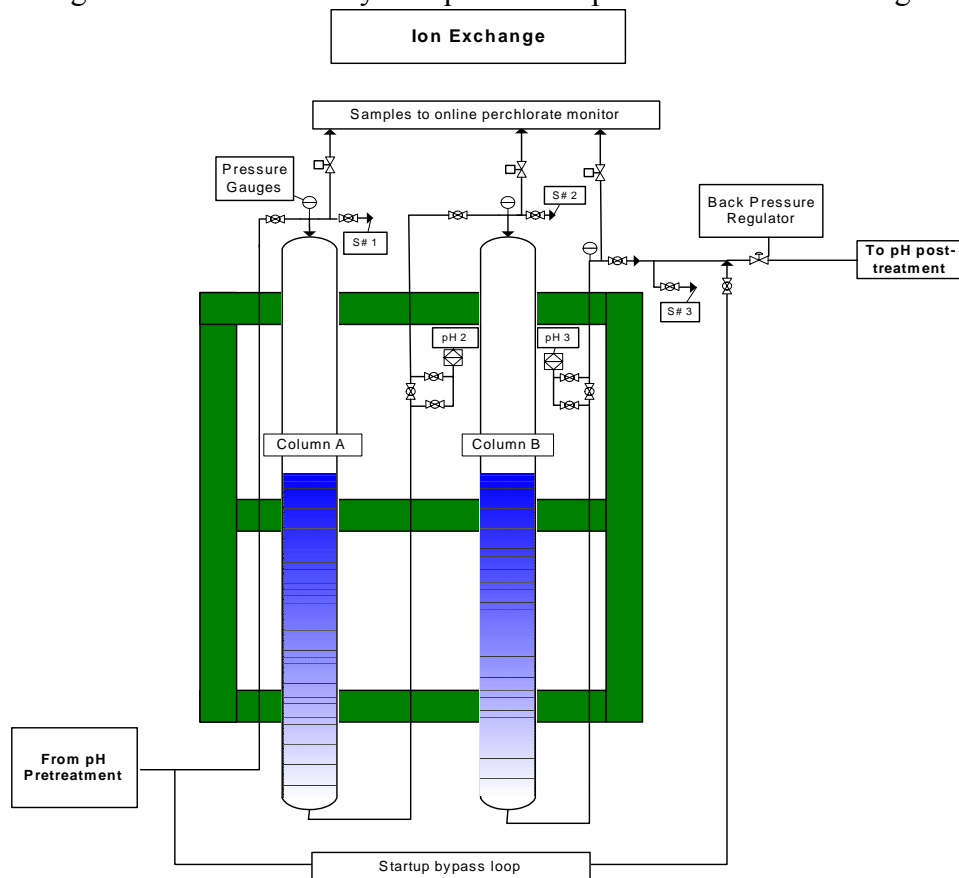


Figure B-4. Ion Exchange

A schematic depicting operation of the perchlorate field monitor is shown in Figure B-5. The field monitor operates using a solid-phase extraction cartridge loaded with styrene-divinylbenzene resin that is preconditioned with decyltrimethylammonium bromide (DAB). DAB is an ion-pairing reagent with a highly specific affinity for perchlorate. Water samples, daily check standards, and/or deionized water blanks are passed through the cartridge, where perchlorate, as well as small quantities of major ions, is retained. A rinse step removes potential interferences. The perchlorate ion-pair is eluted from the cartridge with acetone and delivered to a test-tube mounted in a spectrophotometer. Deionized water, a second perchlorate-specific ion-pair, and xylene are added. This second ion-pair is brilliant green dye, which competes with the DAB for the perchlorate ion-pair. The exchange of perchlorate from DAB to the brilliant green dye is favored because the dye ion-pairs are strongly hydrophobic and are extracted into the layer of xylene. Following a ten minute equilibration time, the absorbance of dye in the xylene layer is recorded. The detection limit for a 250-mL sample is 1 µg/L and the linear range is 1-30 µg/L.

Each day, a blank, mid-range standard, influent, effluents, a standard, and a blank will be run in sequence. The perchlorate concentration will be computed based on the average daily response factors derived from the two calibrations. Results will be stored on-board a lap-top PC that controls the monitor and will be reported daily via modem to ARA. Biweekly maintenance is planned to examine the long-term performance of monitor components, to replace the solid-

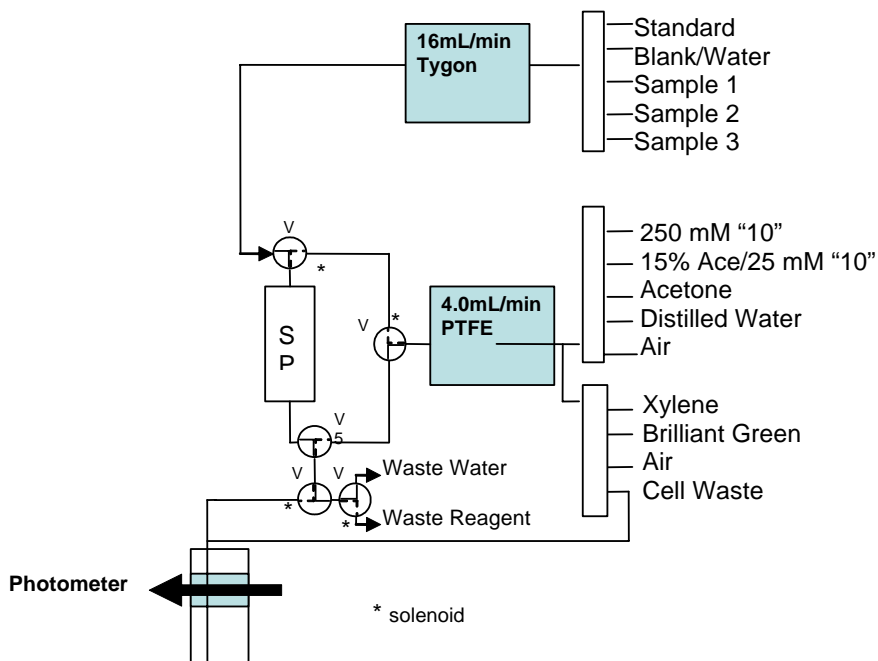


Figure B-5. Field Monitor

phase extraction cartridge, replenish reagents, and dispose of waste. After initial validation of performance, data generated by the prototype perchlorate field monitor will be used to assess the performance of the ion exchange system.

Post Treatment:

Following ion exchange, the treated groundwater will undergo post treatment to neutralize the effluent before discharge (Figure B-6). Neutralization will be accomplished by air stripping carbon dioxide from the effluent and addition of caustic. Adequate residence time (>5hours) will be provided to assure equilibrium is attained. By controlling pH of the effluent, the degree of CO₂ removal and resulting alkalinity can be precisely controlled.

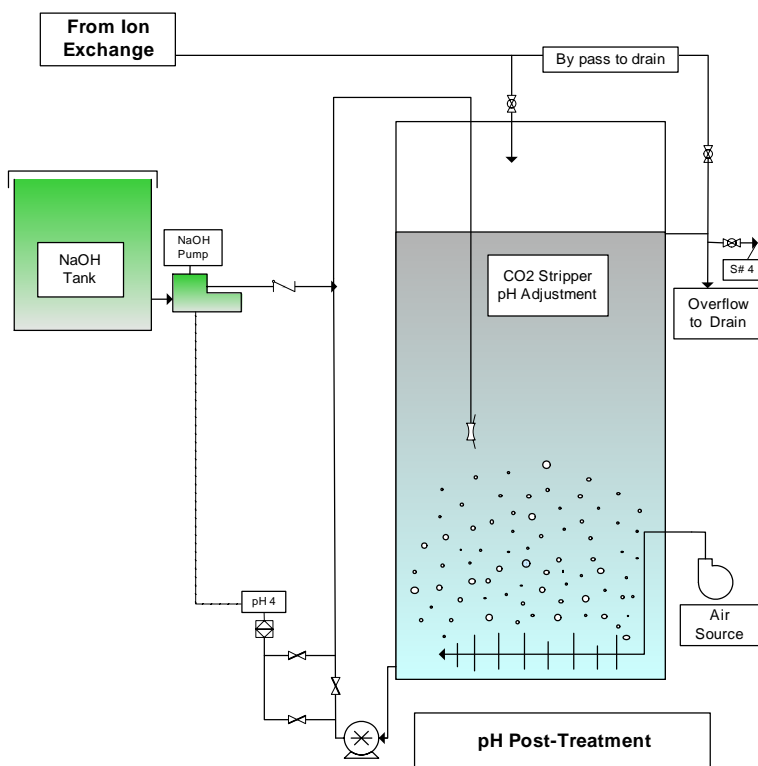


Figure B-6. Post Treatment

Residuals Treatment:

Both biodegradation and super-loading tests will be conducted on spent regenerant from the field demonstration. In addition, two different regeneration techniques will be employed: single-pass and batch regeneration. The regeneration solution will be prepared using two equivalents of 50% sodium hydroxide in five bed volumes of water (approximately 2vol% of 50% NaOH based on a two liter bed volume). Anion and pH analyses will be conducted on each bed volume of spent caustic regenerating solution and rinse water to determine regeneration effectiveness. The residual acid solution used for protonation will be collected and used to neutralize and dilute the spent regenerating solution prior to biodegradation tests. This solution will be prepared using two equivalents of 12N hydrochloric acid in five bed volumes of water (approximately 3vol% of

12N HCl based on a two liter bed volume). If the volume of residual acid is not sufficient for neutralization, concentrated sulfuric acid or hydrochloric acid will be used.

Super-loading tests will be conducted on residuals from the first regeneration test. Since the demonstration-well water has a very high perchlorate concentration, high resin concentration ratios (>20:1) will probably not be attainable. Therefore, the goal for these tests will be to attain a concentration ratio of >10:1. Resin super-loading tests will be conducted on spent regenerant recovered at the maximum strength possible (minimum dilution). Flow tests will be conducted in bench-scale equipment with up to three columns configured in series. Evaluations will be conducted using up to three different resins (PWA2, A-530E, and A-600). A treatment concept will be developed for each resin and operating costs calculated based on actual treatment capacity, resin cost, caustic cost, disposal/incineration cost, and equipment cost. Anion and pH analyses will be conducted on each bed volume of column effluent.

Biodegradation will be demonstrated in bench-scale flow reactors (2.5 liters). ARA's patented suspended-growth, continuous-stirred-tank-reactor (CSTR) technology will be configured similar to existing commercial systems using two reactors in series. Effluent from the second and third column-regeneration tests will be combined to provide enough effluent for biodegradation testing. Even though concentrated spent regenerating solution (~5 BV dilution) can be biodegraded, dilution to a minimum of 10 bed volumes will provide better conditions (TDS <2%) and sufficient effluent for extended biodegradation testing. Spent protonating solution will be used for dilution and partial neutralization to simulate commercial procedures that may be employed to minimize acid and caustic consumption. The volume of effluent from two regenerations (10 BV each) will be approximately 40 liters. This volume provides only 16 days of operation of the biodegradation system at a very conservative residence time of 24 hours. This is a short test for the flow biodegradation system. Addition of effluent from the fourth column-regeneration would extend operation by 50% to 24 days. Also, to ensure meaningful data are obtained during this short test, reactors will be inoculated and adapted to test conditions using a surrogate water prepared to mimic the spent, diluted regenerating solution. After the bioreactors have achieved steady-state operation using the surrogate, the feed will be switched to the actual spent regenerant. Reactors will be sampled and analyzed daily for perchlorate. Operating cost for biodegradation of spent regenerant will include the cost of nutrients, neutralization chemicals, and disposal.

4. Sampling Procedures

4.1 Pilot Field Demonstration

The collection of representative samples during execution of this project is vitally important to the success of project objectives. Sample collection during the field demonstration effort will include groundwater samples (pre- and post-treatment), analyzed by both online and standard laboratory techniques. The schematic shown in Figure B-7 lists the sampling locations of the pilot system. The feed stream and effluent from each column will be monitored daily by the online perchlorate monitor. This information along with operational data such as pH, flow, and pressure will be collected and stored by the data acquisition system. In addition to the online perchlorate analysis, grab samples will be collected at least biweekly for validation of results obtained by the field monitor. A statistical comparison of results by the field monitor versus laboratory results will be made for validation of the performance of the field monitor. The samples collected and analyzed for perchlorate will be used to determine overall contaminant removal and process efficiency. Tables A-1 and A-2 list the frequency of samples to be collected over the duration of the study, and Table B-3 lists the minimum sample volume, holding time, and preservative for each analytical method proposed for use during the field demonstration. The following subsections provide details on sample collection for the field effort.

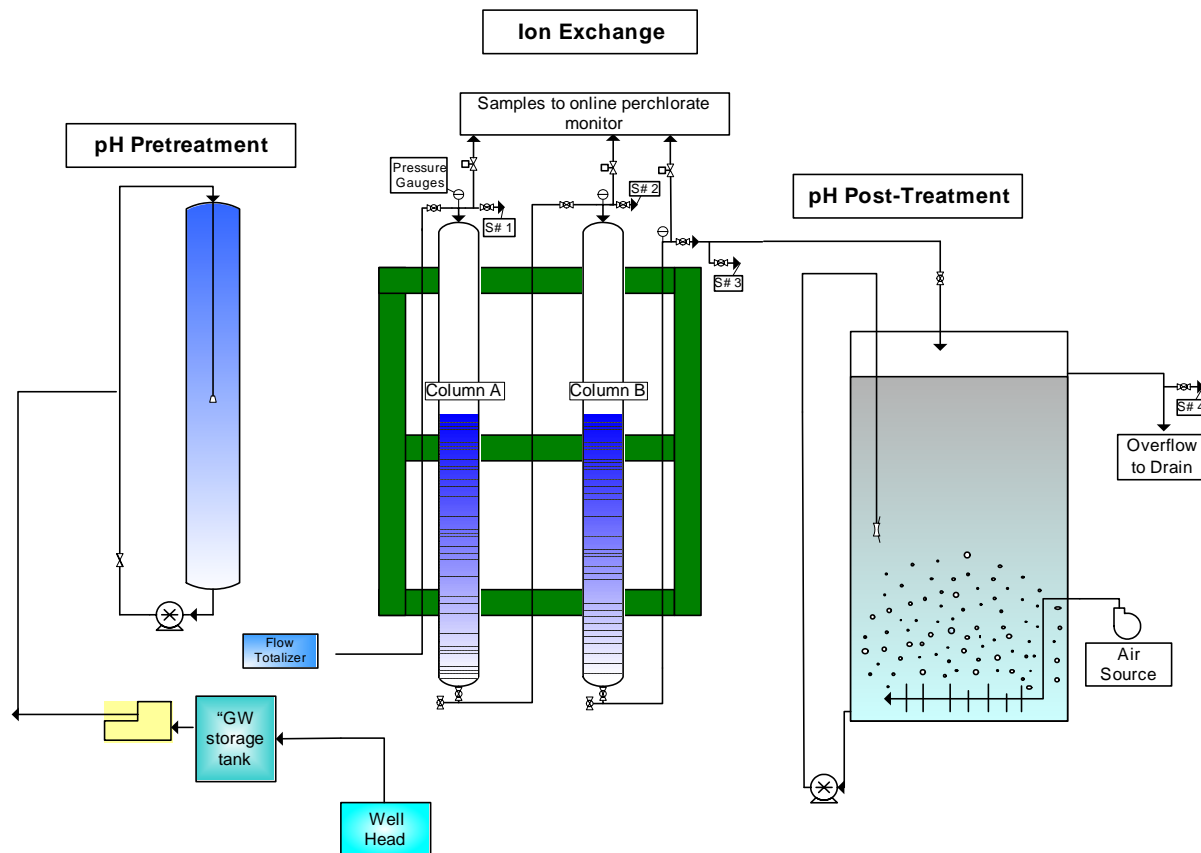


Figure B-7. Pilot System Process Schematic with Sampling Locations

Table B-1. Sampling Summary for ESTCP Pilot Demonstration

Parameter	Sample Point	Sample Frequency	Method	#Samples Collected*
Perchlorate	1,2,3	Daily	Online/Field	336
	1,2,3,4	Biweekly	EPA 314.0	128
Anions	1,2,3,4	Weekly	EPA 300.1	64
pH	1,2,3,4	Continuous	Online/Field	---
General physical	1 and 4	Weekly	Lab	32
VOC	1 and 4	TBD	Lab	TBD

* This is the maximum number of samples that is planned for collection for the analytical parameter over the four month test period. This number does not include duplicates or QA/QC samples collected and analyzed in accordance with the QAPP.

Table B-2 provides a sampling summary for the effluents of regeneration and residual treatment processes. Before initiating any of these processes, the influent will be analyzed to determine initial perchlorate and other anion concentrations as well as pH.

Table B-2. Sampling Summary for Regeneration and Residual Treatments

Process	Parameter	Sample Frequency	Method	#Samples Collected
Regeneration	Perchlorate	Each BV	EPA 314.0	TBD
	Anions	Each BV	EPA 300.1	TBD
	pH	Each BV	SM 4500	TBD
Superloading	Perchlorate	Each BV	EPA 314.0	TBD
	Anions	Each BV	EPA 300.1	TBD
	pH	Each BV	SM 4500	TBD
Biodegradation	Perchlorate	Daily	EPA 314.0	TBD
	Anions	Weekly	EPA 300.1	TBD
	pH & ORP	Daily	Online	TBD

Table B-3. Sample Parameters, Volume, Preservative Requirements and Hold Times

Parameter	Matrix	Method	Volume	Container & Preservation	Hold Time
Perchlorate	Aqueous	EPA 314.0	100 ml	HDPE, Cool 4°C	28 days
Anions	Aqueous	EPA 300.1	100 ml	HDPE, Cool 4°C	28 days
Turbidity	Aqueous	SM 2130B	100 ml	HDPE, Cool 4°C	48 hrs
Color	Aqueous	SM 2120B	50 ml	HDPE, Cool 4°C	48 hrs
Hardness	Aqueous	SM 2340	100 ml	HDPE, Cool 4°C, ph<2, HNO ₃	6 month
Alkalinity	Aqueous	SM 2320B	100 ml	HDPE, Cool 4°C	14 days
Conductance	Aqueous	SM 2520	100 ml	HDPE, Cool 4°C	28 days
pH	Aqueous	SM 4500	5 ml	N/A	Immediate
Solids (TS/TDS)	Aqueous	SM 2540	100 ml	HDPE, Cool 4°C	7 days
Metals (Ca, Cu, Fe, Mg, Mn, K, Na, Zn)	Aqueous	SM 3125	200 ml	HDPE, ph<2, HNO ₃	6 month
VOCs	Aqueous	EPA 8260	40 ml	glass, Cool 4°C, ph<2, HCl, 0.25% Na ₂ S ₂ O ₃	14 days

4.2 Sample Identification, Custody and Transport

4.2.1 Sample Identification

Samples collected in the field will be labeled clearly and legibly. Each sample will be labeled with a unique sample identification number that identifies characteristics of the sample as follow:

Characteristic:	(i)	-	(ii)	-	(iii)	-	(iv)
	Sample ID		Date		Time		Sampler
Example:	1/A		01/01/05		1104		jsb

Where:

Sample ID - 2 characters identifying task (1, 2, 3) and the sample point (A, B, C)

Date - date sampling occurred: (mm/dd/yr)

Time - time sampling occurred (24-hr clock)

Sampler - 3 alpha characters that identifies the sampler (initials)

4.2.2 Preparation of Bottles for Shipment

Preparing bottles for shipment will be conducted in the following manner:

- Label bottles with prepared labels (see 4.2.1) and secured with tape.
- Record the samples on the Chain of Custody forms (see 4.2.3).
- Place sample containers in plastic zip-loc, bubble-pack bags.
- Prepare an empty, clean insulated cooler by removing all existing labels.
- Place 3-4 ice packs in a garbage bag at the bottom of the cooler. Place a second garbage bag inside the first and fill with the sample bottles. Seal the bag with the samples with strapping tape. Add additional bags of ice to the first bag to surround the samples. Seal the outer bag with strapping tape and a custody seal.

4.2.3 Sample Custody

Samples will be retained at all times in the field crew's custody. To accommodate the field schedule, samples will be shipped to the appropriate laboratory as soon as possible by an overnight courier. If samples are collected over the weekend, they will be kept inside so they are protected from direct sunlight and must be shipped on the following Monday. The temperature of all samples shipped will be as close to 4°C as possible.

Sample custody seals will be placed on the outside of each individual container or wrapped around each plastic bag inside the shipment cooler(s). Each custody seal will be attached in manner to allow detection of unauthorized tampering of samples after collection and prior to analysis. The date and initials of the sampler will be recorded on each seal.

Chain of custody (COC) forms will be initiated at time of sample collection. These forms will ensure that all collected samples are properly transferred over from the sampler to the laboratory sample custodian. The following information will be provided when filling out the COC forms (some sections may not be applicable during the field demo):

Table B-4. Chain of Custody Information

Project Name	Enter the project name as it is listed on the contract status summary sheets distributed periodically.
Facility Name, Address, & Phone #	Enter the complete name and correct mailing address for the Demonstration Test Facility.
Field Contact and Phone Number	Enter the complete name of the field sample custodian and a phone number where they can be reached in the field.
Project Manager and Phone Number	Enter the complete name of the project WAM and the phone number where they can be reached.
Laboratory Name, Address, Contact, and Phone Number	Enter the complete name of the laboratory and the ship to address. Also include the contact at the facility and the phone number where they can be reached.
Shipping Method and Air Bill No.	Enter the name of the overnight carrier service used to ship the samples and the complete Air Bill No.
Matrix	Enter the type of sample matrix (i.e., solid, liquid, gas).
Sample Number	Enter the sample identification number.
Date / Time	Enter the data and time of actual sample collection
Parameters	List the parameters to be analyzed. If abbreviations for parameters are used, they need to be explained somewhere on the sheet. Also provide further details for logging in samples
Number of Containers	Enter the total number of containers for a given location.
Observations	Enter any miscellaneous observations or comments to explain sample (i.e. color).
Comments, Special Instructions	For sample handling and analysis. QC samples will be identified here.
Relinquished By:	Sign and enter the complete name of the sample custodian who filled out the chain-of-custody form. Also enter the date and time the form was completed.

When all line items are completed or when the samples are picked up, the sample collection custodian will sign and date the form, list the time, and confirm the completeness of all descriptive information contained on the form. Each individual who subsequently assumes responsibility for the sample will sign the COC form and provide the reason for assuming custody. The field COC terminates when the laboratory receives the samples. The field sample custodian should retain a copy of the COC form for program files.

The COC records will accompany the shipment, or transfer of samples. For site characterization samples being shipped, these documents will be enclosed in a waterproof plastic bag and taped to the underside of the ice chest lid. For shipment of multiple coolers, COC records are prepared separately for the contents of each cooler separately. Each container prepared for shipment will be securely taped shut. Reinforced or other suitable tape (such as strapping tape) will be wrapped around the ice chest. COC seals will be affixed on each ice chest prepared for shipment. When selecting sample shipment modes, field personnel will ensure that the sample will not exceed allowable holding times for individual analyses. When a commercial common carrier is used to ship samples, all samples will be shipped "Priority One/Overnight." When using the commercial carrier, Federal Express, air bills will be completed and attached to the exterior lids of the containers. Samples collected during the field demonstration for analysis by ARA's in-house laboratory will be shipped to:

ARA Associates
430 West 5th Street, Suite 700
Panama City, Florida, 32401
Phone #: 850-914-3188

Field demonstration samples not analyzed by ARA's in-house laboratory will be shipped to the following address:

STL Tallahassee
2846 Industrial Plaza Drive
Tallahassee, FL, 32301
850-878-3994
Attn: Sample Custodian

Any discrepancy between the samples and the chain-of-custody information, any broken or leaking sample bottles, or any other abnormal situations will be reported by the laboratory to the ARA Project Manager (PM). The ARA PM will regularly contact the laboratory during the demonstration to ensure samples are being shipped and analyzed in accordance with QAPP specifications. If required, corrective action options will be discussed and implemented. Notations of the problem and resolution will be made in a laboratory Non-Conformance Record and documented in the analytical report narrative. The information required to be recorded by the sample custodian includes the following:

- Client identifying number or description;

- Project number;
- Date of receipt;
- Client name;
- Analyses required; and
- Condition of sample

Once samples are in the custody of the laboratory, sample integrity will be maintained through the use of locked storage areas. Removal of samples will be documented on the sample log-in sheet or on the computer system. When samples are required for preparation and/or analysis, the sample custodian or designee will distribute the requested samples to the appropriate analysts. An internal COC form will be signed by the individual to whom the samples are relinquished. Documentation in the laboratory will be initiated by the sample custodian who receives the sample, assigns the laboratory numbers (or uses sample ID numbers), and tracks the samples internally.

4.3 Field Documentation

All handwritten documentation must be legible and completed in permanent waterproof ink. Corrections must be marked with a single line, dated, and initialed. All documentation, including voided entries, must be maintained within project files.

4.3.1 Project Logbooks

Project logbooks will be kept on-site during field operations. All activities will be recorded in a bound field notebook of water-resistant paper. Entries will be made legibly, in indelible ink, and will be signed and dated. Information recorded will include:

- Date, time and place of sampling;
- Duplicate samples;
- Site-specific QC samples;
- Data from field measurements (sample location, etc.);
- Sample preservation procedures used if any;
- Calibration activities of health and safety monitoring instruments;
- Sampling procedures;
- Observations about site and samples (odors, appearance, etc.);
- Sampling equipment;
- Decontamination procedures; and
- Health and safety issues.

Observations or measurements taken in an area where contamination of the field notebook may occur can be recorded in a separate bound and numbered logbook before being transferred to the project notebook. The original records will be retained, and the delayed entry will be noted as such.

Field notebooks are intended to provide sufficient data and observations to enable participants to reconstruct events that occur during field activities. The field notebook entries should be factual, detailed and objective.

4.3.2 Corrections to Documentation

Unless restricted by weather conditions, all original data recorded in field notebooks and on sample identification tags, chain-of-custody records, and receipt-for-sample forms will be written in waterproof ink. These accountable, serialized documents are not to be destroyed or thrown away, even if they are illegible or contain inaccuracies that require a replacement document. If an error is made on an accountable document assigned to one person, that individual may make corrections simply by crossing out the error and entering the correct information. The erroneous information should not be obliterated. Any error discovered on an accountable document should be corrected by the person who made the entry. All corrections must be initialed and dated.

5. Testing and Measurement Protocols

During the field demonstration, analysis of samples for perchlorate and anions will be considered critical for the purposes of this QAPP. Samples will be collected as described earlier in section 4 and analyzed in accordance with the procedures referenced and described below. Table B-5 summarizes the methods to be used during this study.

Table B-5. Analytical Parameters for the Proposed Study

Parameter	Matrix	Lab	Method	Method Type
Perchlorate*	Aqueous	ARA	EPA 314.0	Ion Chromatograph
Perchlorate*	Aqueous	ARA	Online monitor	SPE/Colorimetric
Anions	Aqueous	ARA	EPA 300.1	Ion Chromatograph
pH	Aqueous	ARA	SM 4500	Electrometric
Turbidity	Aqueous	NELAC Certified	SM 2130B	Nephelometric
Color	Aqueous	NELAC Certified	SM 2120B	Visual Comparison
Hardness	Aqueous	NELAC Certified	SM 2340	Titration
Alkalinity	Aqueous	NELAC Certified	SM 2320B	Titration
Conductance	Aqueous	NELAC Certified	SM 2520	Electrometric
Solids (TS/TDS)	Aqueous	NELAC Certified	SM 2540	Gravimetric
Metals (Ca, Cu, Fe, Mg, Mn, K, Na, Zn)	Aqueous	NELAC Certified	EPA SM 3125	ICP/MS
VOCs	Aqueous	NELAC Certified	EPA 8260	GC/MS

Notes: * Critical compound for performance validation is perchlorate.

The following paragraphs summarize the laboratory protocols and calibration requirements for the critical measurements.

5.1 Laboratory Protocols

The critical parameter for this study is the analysis of anions – specifically perchlorate– in groundwater. Throughout the demonstration, the concentration of the anions will be monitored to assess the performance of the technology.

5.1.1 Inorganic Anions by Methods 300.1 (anions) and 314.0 (perchlorate)

These methods cover the determination of inorganic anions in surface water, groundwater, and drinking water. A volume of sample ranging from 10-1000ul is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector. The methods differ by the size of the sample loop, the column used, and the mobile

phase selected to elute the anion of interest from the analytical column. When various contaminants are present at different orders of magnitude, the laboratory will perform analyses using multiple dilutions of the sample as necessary to quantitate the compound at higher concentrations and still achieve low detection limits for other compounds. Inorganic anions analyzed by EPA 300.1 and 314.0 will be calibrated in accordance with method requirements.

An analysis batch will consist of no more than 20 samples. These included the field samples as well as any QA/QC check samples. Within the analysis batch, for every group of ten field samples, at least one Lab Reagent Blank (LRB) and Continuing Cal Check Standard (CCAL) must be analyzed. The CCAL should consist of a mid-point standard, prepared fresh from the calibration standard stock. An initial calibration will be performed using 5 standards at concentrations ranging from the reporting detection limit (RDL) to the upper limit of linearity. Routine initial calibration (ICAL) criteria will be met with the additional requirement that the linearity criteria of RSD <20%. The continuing calibration standard (CCAL) analyzed every 10th field sample and must meet routine CCAL requirements.

5.1.2 Perchlorate by On-line Monitor Technique

This method covers the determination of perchlorate in an aqueous solution with pre-concentration using solid-phase extraction (SPE), subsequent elution, and a colorimetric detection. This analysis will be performed with a proprietary technique and equipment developed by ARA. A SPE cartridge loaded with styrene-divinylbenzene resin is preconditioned with decyltrimethylammonium bromide (DAB), an ion-pairing reagent with a highly specific affinity for perchlorate. Sample at a flow rate of 10 ml/min is passed through the cartridge, where perchlorate as well as small quantities of major ions are retained. A rinse step removes potential interferences. The perchlorate ion-pair is eluted from the cartridge with acetone and delivered to a test-tube mounted in a spectrophotometer. Deionized water, a second perchlorate-specific ion-pair and xylene are added. This second ion-pair is Brilliant Green dye, which competes with the DAB for the perchlorate ion-pair. The exchange of perchlorate from DAB to the dye is favored because the dye ion-pairs are strongly hydrophobic and are extracted into the layer of xylene. Following a ten minute equilibration time, the absorbance of dye in the xylene layer is recorded.

The detection limit for a 250-mL sample is 1µg/L and the linear range is 1-30 µg/L. The analysis cycle time is approximately 45 minutes if a 250 ml sample is taken. Due to this time restraint, a blank, a check standard, groundwater feed, lead IX column effluent, lag IX column effluent, 2nd check standard and final blank will be run in sequence each day. The perchlorate concentration will be computed based on the average daily response factors derived from the two calibration check standards. Results will be stored on-board the lap-top PC that controls the monitor and will be reported daily via modem to ARA. Biweekly maintenance is planned to examine the long-term performance of monitor components and to replace the SPE, replenish reagents and dispose of waste. As the demonstration progresses, data will be generated from this prototype monitor that will eventually be the basis for

routine performance assessments. Results from the online monitor will be compared with analysis results generated by EPA 314.0 perchlorate IC method.

5.1.3 External NELAC Certified Laboratory Analysis

The additional non-critical analytical procedures listed in Table B-3 are to be performed by a NELAC Certified Laboratory in accordance with approved Standard Methods for the examination of water. The QA/QC standards specified under each method will be followed and documented by the laboratory. A detailed report including QA/QC results will be included with the submission of all analytical results.

6. QA/QC Checks

For this project, QA objectives have been established to ensure that data generated are of adequate quality to achieve technical objectives. The QA objectives for the critical data collected during the demonstration are presented in Table B-6. Acceptance criteria for accuracy, precision, and completeness are listed, along with the expected detection limit of the devices used to take the critical measurements. Overall, QA objectives for non-critical parameters are also noted as guidelines. The discussion below includes a summary of how these objectives will be assessed in the laboratory. Specific QC check procedures for critical measurements are discussed in section 6.2; including corrective actions to be taken in the event these QC checks do not meet criteria.

6.1 QA Objectives

Critical measurements for this project are inorganic anions, primarily perchlorate. Table B-6 summarizes QA objectives for all parameters to be analyzed, with the achievement of these objectives for the critical parameters discussed below.

Precision for anions will be assessed by the analysis of duplicate matrix spikes (MS/MSDs) performed on select project samples to determine the reproducibility of the measurements. The relative percent difference (RPD) between the spiked sample concentrations will be compared to the objectives given in Table B-6. Precision for non-critical parameters will be assessed by the routine QC associated with the analytical batch (duplicate samples analyzed using project or non-project samples run in the same batch as the project samples).

Accuracy objectives for anions are evaluated by the percent recovery of the MS/MSDs performed using project samples. A Laboratory Control Sample (LCS), or spike in a blank, will be analyzed with each MS/MSD to confirm analytical accuracy in the absence of matrix effects. These analyses are discussed further in the following subsection.

Table B-6. QA Objectives for Critical Parameters

Parameter	Matrix	Type (1)	Method	Precision (2)	Accuracy (3)	RDL (4)	Units
Perchlorate	Aqueous	C	EPA 314.0	20	80-120 %	5.0	ug/L
Anions (Nitrate, Sulfate)	Aqueous	NC	EPA 300.1	20	80-120 %	1.0	mg/L
Perchlorate	Aqueous	C	online	25	-	1.0	ug/L

Notes: (1) Parameter type is C=critical, NC=non-critical.
 (2) Precision is assessed by RPD between the MS/MSD pair or by a sample and duplicate.
 (3) Accuracy objectives are based on the % recovery of spiked samples.
 (4) The RDL (reporting detection limit) is based on the lowest calibration standard.

Detection limits for this project are defined as the reporting limit (RDL) as determined by the lowest concentration standard meeting the specified calibration criteria. For the inorganic anion determinations, the detection limit of perchlorate on an undiluted aqueous sample will be set at 5.0 ppb by EPA Method 314.0, and 1.0 ppb by the on-line method under evaluation. Detection limits will be adjusted as necessary based on the matrix and the need for dilution or by the amount of sample concentrated with the on-line method. Method detection limits are derived based on the analysis of 7 replicate low-level standards and the standard deviation (SD) of the results: $MDL = 3SD$.

Comparability is based on the use of established, EPA-approved methods for the analysis of the critical parameter, as well as most non-critical parameters.

Representativeness is achieved by collecting samples representative of the matrix at the time of collection. For the aqueous samples critical to this project, this is achieved by the collection of an aliquot of well-mixed sample.

6.2 QC Checks

General QA objectives have been discussed in the preceding paragraphs. The following QC check procedures will be utilized to assess the precision and accuracy of the measurements associated with the critical parameters. The required QC samples include: Lab Reagent Blank (LRB), Initial Cal Check (ICAL), Lab Control Sample (LCS), Continuing Cal Check (CCAL), and Field Duplicate (Dup). These checks are summarized in Table B-7, and are discussed further below.

Calibration criteria were described earlier in section 5.1. In addition to calibration requirements, inorganic anion analysis will include the analysis of MS/MSD samples that are prepared using project samples, and designated at a frequency of 5 % of the samples. Samples will be spiked by the addition of approximately 5 times the native sample concentration, as estimated based on historical data or after screening the primary sample. The sample, MS and MSD will all be analyzed in the same batch at the same dilution, even if this requires reanalysis of the primary sample. If the initial spike preparation results in spiking levels that are inappropriately low relative to the native sample concentration, the three samples (primary, MS and MSD) will be analyzed with each spiked pair. If the results of both the LCS and the MS/MSD do not meet criteria, analysis will stop until the problem is identified and corrected. If one or the other fails, but not both, the laboratory analyst will contact the QA Coordinator to discuss and determine the appropriate corrective action.

Table B-7: QC Checks for Critical Anion Analysis

QC Check	Frequency	Criteria	Corrective Action
ICAL	Initially and as needed;	RSD <20%; EPA 300.1 criteria (see method)	Reanalyze calibration; prepare new standards as necessary
CCAL	Every 12 hours	RF <20% RPD,	Rerun CCAL standard; recalibrate if needed
Method blank	Every 12 hours	< RDL (for critical cpds)	Rerun; system maintenance
MS/MSD	As per COC or 5%	<u>Aqueous</u> : % recovery 80- 120; 20% RPD;	Reanalyze sample and spikes; if still fails, flag data; if LCS also fails - stop analysis and contact QAC
LCS	With each MS/MSD	% rec. = 80-120	Reanalyze; if LCS and MS/MSD fails stop analysis and contact QAC
Field duplicates	As per sampling schedule	<u>Aqueous</u> RPD < 20 %;	Flag data

7. Data Reporting, Data Reduction, and Data Validation

For data to be scientifically valid, legally defensible, and comparable, valid equations and procedures must be used. Evaluation of measurements is a systematic process of reviewing a body of data to provide assurance that the quality of the data is adequate for its intended use. The following sections describe the data reporting, data reduction and data validation procedures to be used for laboratory data.

7.1 Laboratory Reporting

Laboratory reports will include tabulated results of all samples. The final report will also include method summaries, detailing any deviations or modifications of the proposed methods. Data will be submitted in a report with sufficient detail such that independent validation of the data can occur. Raw data will include any calibration information, instrument printouts, lab bench sheets, sample preparation information, etc. The completed report will be reviewed by the laboratory QA manager, and approved by the laboratory project manager (or their designees) prior to submission.

7.2 Data Reduction

All data reduction will be completed as specified in the appropriate method. Where data reduction is not computerized, assumptions and calculations will be recorded on the raw data printouts, on pre-printed bench sheets, or in permanently bound notebooks. The data reduction for some analyses includes analysts' interpretations of the raw data and manual calculations. When this is required, the analysts' observations will be written in ink on the raw data sheets. Any corrections to data sheets will be made by lining out inaccurate information, dating and initialing the line-out, and adding the revised information next to the line-out.

7.3 Data Validation

Data generated in each analytical section shall be reviewed by the analytical task leader on a daily basis for completeness. The personnel involved at each stage in data reduction, validation and reporting are shown in Section 2-2. Data will be reported in standard units, as described above. Data validation begins with the analyst and continues until the data are reported. The analysts will verify and sign the appropriate forms to verify the completeness and correctness of data acquisition and reduction. An independent reviewer will review this information to ensure close adherence to the specified analytical method protocols. All instrument systems must be in control and QA objectives for precision, accuracy, completeness, and method detection limits must be met. In the event that data do not meet the project objectives, the sample shall be reanalyzed or re-extracted. If the sample still does not meet project requirements, the QA Coordinator shall be notified immediately. The problem(s) will be discussed and appropriate corrective action shall immediately be implemented. If project objectives have been impacted, or changes were required in analytical procedures, these modifications will be clearly noted in the Final Report.

The principal criteria that will be used to validate the integrity of data during collection and reporting are as follows:

- Verification by the project analyst that all raw data generated for the project have been documented and stored. Storage locations must also be documented in the laboratory records;
- Examination of the data by the laboratory manager or his or her designee to verify adequacy of documentation and agreement with method protocols; and
- Reporting of all associated blank, standard, and QC data, along with results for analysis of each batch of samples.

Analytical outlier data are defined as those QC data lying outside a specific QC objective window for precision or accuracy of a given analytical method. Should QC data be outside of control limits, the laboratory supervisor will investigate the potential causes of the problem. Corrective action (as discussed and tabulated in section 6) will be initiated as necessary, documented, and if unresolved the data will be reported flagged with a data qualifier.

7.4 Data Storage Requirements

The subcontracted analytical laboratories will be responsible for storing on disc all raw data for five years. ARA and/or its subcontractors will retain all hard copies of the analytical data for a period of five years. ARA and/or its subcontractors will also retain the field log books and other correspondence and deliverables for five years.

7.5 Final Technical Reports

The validated field and analytical data will be used to prepare the Technical Evaluation Report, evaluating the field and bench studies and assessing the technologies studied potential for full scale application. The report will contain, at a minimum, the information requirements as specified in the ESTCP guidance document. The report will include a QA review and discussion as a separate and identifiable section. This review will include, at a minimum, the following information:

- A discussion of the procedures used to define data quality and usability and the results of these procedures. The discussion will focus on the data quality indicators such as precision, accuracy, completeness, comparability and representativeness and will include summary tables of the QC data obtained during the demonstration. Results will be compared to the data quality objectives set forth in the QAPP to provide an assessment of the factors that contributed to the overall quality of the data.
- The results of any technical systems and/or performance audits performed during the course of the project will be documented, including corrective actions initiated as a result

of these audits and any possible impact on the associated data. If any internal audits were performed, these too will be reviewed.

- All changes to the original QAPP will be documented regardless of when they were made. The rationale for the changes will be discussed along with any consequences of these changes.
- The identification and resolution of significant QA/QC problems will be discussed. Where it was possible to take corrective action, the action taken and the result of that action will be documented. If it was not possible to take corrective action (for example, a sample bottle was broken in transit), this, too will be documented.
- A discussion of any special studies initiated as a result of QA/QC issues and/or corrective actions, including why the studies were undertaken, how they were performed and how the results impacted the project data.
- A summary of any limitations on the use of the data will be provided including conclusions on how these constraints affect project objectives.

The QA section will provide validation of the measurements used in the demonstration (and subsequent acceptance/rejection) of this technology. This section (and the final report) will be subject to review by the, QA, and Program Managers. This review will assess the assumptions made in evaluating the data and the conclusions drawn. The Program Manager must approve the reports prior to release.

8. Assessments

A quality assurance audit is an independent assessment of a measurement system. QA audits may be internal or external audits and performance or system audits. Internal laboratory audits are conducted by the project laboratory's QA/QC coordinator and may be functionally independent of the sampling and analytical teams. External audits are those conducted by an independent organization, such as ESTCP. For this project there will be an internal systems audit conducted by the QA Manager during the field demonstration of the laboratory performing the critical analysis. Performance and system audits are described below.

8.1 Performance Audits

Performance audits are intended to quantify performance of the total measurement system. These types of audits often include performance evaluation samples supplied by an independent regulatory agency. This type of audit is not envisioned for this project.

8.2 Systems Audits

Systems audits will be conducted on sampling/analysis activities by the QA Manager or his designee. These audits are designed to ensure systems are in place for satisfactory sampling and analysis as designated in the QAPP. As appropriate, those audits will consist of any or all of the following items:

- Review the organization and responsibilities to determine the functional operation of the quality assurance program.
- Determine if standard operating procedures are available and implemented as written or as specified in the QAPP.
- Assess traceability of samples and data.
- Determine if appropriate QC checks are being made and that appropriate documentation is maintained.
- Determine if the equipment specified is available, calibrated, and in proper working condition.
- Assure records are properly maintained, including notebooks, log sheets, bench sheets, and tracking forms.
- Verify use of appropriate chain of command methods in responding to variances and implementing corrective action.
- Prepare a project and QA report as designated in the laboratory scope of work to be submitted to the Project Manager and the QA Manager.

8.3 Corrective Action

Corrective actions will be taken upon identification of any problems with the project that affect product quality. The initial line of responsibility for identifying the causes of laboratory problems lies with the analyst, who along with the Laboratory QA Manager or Laboratory Technical Manager will work towards developing a solution. Field personnel who identify a problem with data collection activities will report the difficulty to the Project Manager (PM) or QA Coordinator. The root cause(s) of the problem will be determined, and its effect on the program will be identified. The QA/QC Coordinator and appropriate manager (e.g., laboratory coordinator) and, if necessary, the Program Manager, will develop a corrective action.

As data problems arise, the contractor team will investigate the problems and perform one or more of the following actions:

- If the problem occurs in the field, the field manager will try to correct the problem. If the field manager cannot correct the problem without loss of field data or samples, he/she will immediately contact the Project Manager or QA Coordinator for additional instructions.
- If the problem occurs in the laboratory, the laboratory supervisor will try to correct the problem. If the laboratory supervisor cannot correct the problem without loss of analytical data of known quality, he or she will immediately contact the laboratory project manager and/or their respective QA coordinator for additional instructions.

8.3.1 Corrective Action for Performance/Systems Audits

As noted above, field and laboratory activities will be audited to ensure that required field and laboratory procedures are being followed. If deficiencies or problems are discovered during the audit, the appropriate QA/QC coordinator or their designees will prepare a corrective action memorandum to document the procedures to be implemented to correct the deficiency.

8.3.2 Corrective Action for Data Outside Control Limits

If at any time the data fall outside previously designated limits, the following actions will be taken:

- If instruments are not within calibration limits, the instruments will be recalibrated; samples will be reanalyzed once an acceptable calibration has been obtained.
- If a field/laboratory person or engineering staff member observes data problems (for example, if results for specific QC analysis are outside the QC limits), he or she will immediately notify the appropriate QA/QC coordinator or project director. A determination will be made on the impact of the problem on the data quality and whether any corrective action should be taken.
- If a field/laboratory person observes procedures not being done in accordance with the QA Project Plan he or she will immediately notify the appropriate QA/QC coordinator or project director.

Appendix C

Health and Safety Plan

for the

ESTCP Field Demonstration

at

Redstone Arsenal – Huntsville, Alabama

May 25, 2005

ESTCP PROJECT NUMBER CU-0312
ARA PROJECT NUMBER 16623

Approvals

The undersigned have read and understand the pertinent health and safety procedures and plans applicable to this site.

Andrea Davis
ARA Project Manager

Jeff Rine
ARA Field Manager

Robert Girvin
ARA Health and Safety Reviewer

1. Introduction

Scope and Applicability

This Health and Safety Plan (HASP) applies to field activities conducted by Applied Research Associates, Inc (ARA) in support of the ESTCP Field Demonstration at Redstone Arsenal (RSA), Huntsville, Alabama. The information provided in this plan was developed for the purpose of assigning responsibilities, establishing personal protection standards and mandatory safety procedures, and to provide for contingencies that may arise while operations are being conducted by personnel supporting the ESTCP Field Demonstration at RSA. ARA disclaims responsibility for any other use of this information other than the express purpose for which it is intended and assumes no liability for the use of this information for any other purpose. The evaluations of potential hazards and their controls reflect professional judgments subject to the accuracy and completeness of information available when the plan was prepared. The plan is written for specific site conditions, purposes, dates, and personnel, and must be amended if conditions change during the course of the demonstration.

1.2 Demonstration Work Scope Overview

This demonstration will evaluate and demonstrate the performance of selective ion exchange resins in removing perchlorate from contaminated groundwater and demonstrate efficient destruction of perchlorate in spent regenerating solutions. This demonstration will also evaluate the performance of an economical field monitor capable of on-line, real-time perchlorate analysis.

The project and objectives have been fully described in the Demonstration Plan and the Quality Assurance Project Plan (QAPP). This HASP is designed to cover operation, sampling and related activities during the field demonstration at the site and to assure safe and healthful working conditions. The following items are covered in the HASP:

- Project Organization and Responsibilities
- Task Description
- Hazard Analysis
- Hazard Monitoring and Control
- Emergency Response
- Spill Containment
- Recordkeeping

2. Project Organization and Responsibilities

2.1 Project Organization

The ARA project team will consist of Ed Coppola, Steve Baxley, Jeff Rine, Andrea Davis, Robert Girvin, and Phil Thorne. The Project Manager (PM) is ultimately responsible for the well being of all field personnel under his supervision. To assist him with health and safety related issues and activities, he will designate a Site Safety Coordinator (SSC) to ensure that the HASP is implemented. The SSC has the authority to stop project activities or evacuate the site if hazardous conditions are encountered or if any operation threatens work personnel/public health or safety.

The Field Manager, also appointed by the PM, is responsible for directing field activities and ensuring that personnel follow all sampling and analysis protocols. The Field Manager defers to the SSC for health and safety and compliance. Additional responsibilities for ARA project management personnel and support staff are described in the ARA Environmental Compliance and Health and Safety (EC&HS) Program Manual.

Key personnel, and their responsibilities for the Field Demonstration at RSA are identified in the QAPP, which is a component of the overall Field Demonstration Plan. The ARA Environmental Compliance and Health and Safety Manual specifies the health and safety responsibilities for the Project Manager, Andrea Davis, and the Health and Safety Officer (HSO), Mr. Lew Vereen; therefore these positions are not described here.

2.2 Responsibilities

All persons involved in this demonstration shall read and sign this safety plan prior to performing field investigation activities at Redstone Arsenal in Huntsville, Alabama. Through their signature, personnel indicate that they understand and will adhere at all times to ARA and OSHA requirements presented or referenced in this plan. The designated PM will hold a master copy (with signature sheet) of this plan and a copy will be available at the work site. In addition, all personnel will sign a master signature sheet (Attachment 1) upon arrival, acknowledging that each individual has read, understands, and will comply with the requirements of this Health and Safety Plan. The health and safety-related responsibilities of the various personnel involved in this project are described in the paragraphs below.

Field Manager: The Field Manager is responsible for supervision of all activities when on-site, and for compliance with Quality Assurance (QA) and safety requirements. The demonstration is designed for periods of unattended operation, during which operation variables including pressure, pH, total flow rate, and perchlorate concentration will be monitored remotely. At least once per week, the Field Manager will carry out sampling and system maintenance. The health and safety responsibilities of the Field Manager during site visits include the following:

- Report any health and safety violations or incidents to the Program Manager and Site Safety Coordinator (SSC). A copy of an incident report form is provided in Attachment 2. The incident report includes the following information:
 1. Date, time, and place of occurrence;
 2. Person(s) involved;
 3. Type of incident;
 4. Description of incident and action taken; and
 5. Recommendations to prevent a similar occurrence.

Site Safety Coordinator: The Site Safety Coordinator (SSC) will oversee the safety activities associated with the project. Mr. Robert Girvin will serve as the SSC for the field demonstration project at Redstone Arsenal. His specific responsibilities will include:

- Participating in the preparation and implementation of the HASP and assuring that all personnel have access to the HASP;
- Conducting routine inspections to assure that all the requirements of the HASP are rigorously followed throughout the field activities and documenting environmental compliance and health and safety violations, deviations from the HASP, and hazardous conditions;
- Conducting safety meetings, as necessary, for all site personnel, and completing the Site Safety Briefing Report;
- Halting ARA site operations, if necessary, in the event of an emergency or to correct unsafe work practices;
- Consulting with the Health and Safety Officer before making any amendments to the HASP. The amendments may include upgrading or downgrading PPE, air monitoring for specific compounds, air monitoring frequency, etc.
- Ensuring that protective clothing and equipment are properly used and maintained;
- Overseeing the record keeping for occupational illnesses and injury, individual site assessments, and exposure and monitoring results;
- Obtaining and coordinating emergency assistance;
- Monitoring site conditions and, if determined to be unsafe, authorizing the temporary suspension of operations until the unsafe circumstances have been resolved;

- Preparing and submitting incident reports;
- Ensuring that personnel conducting the field activities have completed the appropriate training and have received medical clearance as applicable; and
- Conducting a post-field activity briefing at the end of the project to identify problems encountered and lessons learned, and preparing a record summarizing actions taken to ensure compliance with applicable requirements at the site.

Field Team Members: All field team members will be comprised of personnel approved by ARA and RSA. All field team members are responsible for protecting their own health and safety to the best of their abilities and each assumes the following responsibilities:

- Review and sign the HASP;
- Wear and maintain personal protective equipment as specified in the HASP;
- Abide by the rules presented in the site HASP and maintain possession of the plan while at the site;
- Take all precautions to prevent injury to themselves and their coworkers and have a thorough knowledge of specific emergency response procedures for their specific work sites;
- Perform only those tasks that they believe they can do safely; and
- Notify the Project Manager and Site Safety Coordinator of any health and safety hazards or violations observed or inadequately controlled by procedures contained in the HASP.

3. Task Description

3.1 Project Objectives

This project will evaluate and demonstrate the performance of selective ion exchange resins in removing perchlorate from contaminated groundwater and demonstrate efficient destruction of perchlorate in spent regenerating solutions. This project will also demonstrate the performance of an economical field monitor capable of on-line, real-time perchlorate analysis. Detailed objectives can be found in the Demonstration Plan.

3.2 Field Activities

This HASP covers field activities associated with the ion exchange technology demonstrated by ARA at Redstone Arsenal. The ion exchange system and field monitor with associated equipment will be constructed and integrated together at ARA's Panama City Research Facility. Once constructed, the system will be installed in an eight by twenty feet enclosed mobile trailer, and a series of functional tests will be performed prior to field mobilization. After sufficient functional testing the mobile pilot system will be transported and put in place, adjacent to the selected well head, at Redstone Arsenal. The enclosed trailer will provide breakered power, climate control, and protection from the elements while in the field. Since the main components of the process are contained within the trailer setup at the site should go relatively smooth and quick.

It is anticipated that the system will be manned full time for a set-up and start-up period (~ 2 weeks). Following this start-up period, a data acquisition system will be used to allow remote monitoring of real-time, key performance parameters (i.e. operation pressures, pH, total flow, and perchlorate concentrations). Site visits will be conducted at least once every week for split sampling and system check/maintenance. Arrangements have been made for an on-sight technician who can rapidly respond to operational or data acquisition anomalies. This technician may also conduct unscheduled site visits following power failure due to thunderstorms or other unforeseen events to inspect and ensure system operation. The following table describes expected activities that may be conducted during site visits.

Table C-1. Field Activity Examples

Field Activity	Description
System Inspection	Upon arrival and departure, visually inspecting exterior and interior of trailer for anomalies or damages. Securing trailer.
Equipment Inspection / Calibration	Ensuring all pumps, pressure gauges, flow totalizers, pH meters, etc, are operating properly. Calibrating, if necessary.
Maintenance	Checking fluid levels of required solutions and adding more, if needed
Sampling	Collecting groundwater and effluent samples
Column Exchange	Replacing a spent column with a regenerated column

4. Hazard Analysis

4.1 Potential Chemical Exposures

Based upon the proposed work plan for the field demonstration, the primary chemicals of concern are acids and bases used for operational control of the process and organic solvents used with the perchlorate field monitor. Another potential exposure hazard is TCE, which is present in the groundwater as a contaminant. The specific chemicals of concern are:

- Sulfuric Acid
- Hydrochloric Acid
- Sodium Hydroxide
- Acetone
- Xylene
- TCE present in groundwater

The chemicals and compounds listed above pose potential health hazards via inhalation, dermal contact or absorption, and ingestion. Some are also suspected or known to be carcinogenic, mutagenic, or toxic. Dermal exposure may result in skin and mucous membrane irritation, as well as internal injury or illness due to absorption. Dermal protection is accomplished by limiting contact with material through the use of personal protective equipment (PPE), and by decontamination and personal hygiene protocols. Ingestion hazards are controlled by strict limitations on eating, drinking, smoking, and by rigorous application of decontamination and personal hygiene protocols. The exposure limits for chemical hazards that may be encountered during the execution of the field demonstration at RSA are given in Table 4-1. The specific types of PPE that will be used are discussed in Section 5.2.

Table C-2. Chemical and Physical Properties for Chemicals of Primary Concern

Contaminant	PEL (ppm)	TLV (ppm)	Skin Notation (Yes/No)	Vapor Pressure @ 23° C & 760 mm Hg	IDLH (ppm)	Flash Point (°F)
Xylene	100	100	No	18	900 Ca	77
Acetone	1000	500	No	180	2500	0
Sulfuric Acid	1000	200	Yes	1	15,000	ND
Hydrochloric Acid	5	2	Yes	167	50	ND
Sodium Hydroxide	2000	2000	Yes	14	10,000	ND
Trichloroethylene	100	50	No	60	1000 Ca	ND

NA = Not Available ND = None Ca = Suspected or Confirmed Animal or Human Carcinogen

4.2 Radiological Hazards

No radiation hazards have been reported for the site and none are expected for the sampling activities.

4.3 Physical Hazards

The physical hazards that may be encountered during the field activities include hazards associated with:

- Existing objects and terrain;
- Lifting heavy objects;
- Personal protective equipment;
- Solar non-ionizing radiation; and
- Other physical hazards.

Existing Objects and Terrain: Existing objects and terrain can present hazards in the form of:

- **Holes, ditches and canals;**
- **Precariously positioned objects (e.g., drums, cables, boards) that may fall or cause an individual to trip;**
- **Sharp objects and rubble such as nails, metal shards, rebar, and broken glass; and**
- **Slippery surfaces.**

Lifting Heavy Objects: Personnel may be exposed to injury caused by lifting heavy objects. Mechanical and hydraulic assists as well as a helper will be used whenever possible to minimize lifting dangers. Useful guidelines for lifting include:

- If possible, lift with your legs, not your back, but always maintain a stable, comfortable posture;
- Lift heavy objects slowly and deliberately, not with a grab and jerk motion; and
- Avoid turning while lifting; turn while you are erect.

Personal Protective Equipment: Personal protective equipment can restrict visibility and movement. This increases the risk of tripping, falling over, falling into floor openings, or striking, or being struck by objects. Personal protective equipment increases the risk of heat stress and reduces workers' ability to move freely and hear direction and noise that might indicate a hazard. This potential hazard will be addressed specifically during safety discussions.

4.4 Other Physical Hazards

Other physical hazards include heat stress, which is a concern especially in summer months. Exposure to hot temperatures increases the likelihood and potential for worker disorders or conditions that could result in injury or illness. Extreme high temperatures may not be the only

element necessary to create the potential for heat exposure disorders or conditions; strong wind accompanied by cold temperatures can also lead to illness or injury. Common heat disorders or conditions include heat stroke and dehydration. Contributing factors to these disorders or conditions are:

- Elevated Temperatures;
- Exposure to humidity;
- Inadequate fluid intake;
- Inappropriate clothing; and
- Poor worker health.

The SSC should monitor daily weather conditions and prescribe appropriate clothing and work-rest schedules as required to minimize the possibility of heat stress-related problems. In addition adequate fluid will be made available for worker to remain full hydrated. Table 4-2 gives the recommended time limits for working in various low temperature ranges.

Table C-3. Maximum Daily Time Limits for Exposure at High Temperatures

Temperature Range		Maximum Daily Exposure
Celsius	Fahrenheit	
0 to 38	32 to 100	No limit, providing that the person is properly clothed and hydrated
>38	>100	Total work time: 8 hours. Alternate 1 hour in and 1 hour out of the high-temperature area.

Early recognition of symptoms associated with heat exposure is essential in preventing serious or permanent disorders or even death. Workers and managers involved in hot weather operations should be adequately trained to recognize the following conditions and related symptoms:

- Heat Stroke - The symptoms of this condition are fatigue, dizziness, nausea or vomiting, headache, shallow or rapid breathing, high body temperature (106-112), rapid heart beat, and decreased alertness or loss of consciousness. Severe shaking of rigid muscles may be caused by a burst of body energy and changes in the body's chemistry. Vague or slow, slurred speech, memory lapses, incoherence, and drowsiness are some of the additional symptoms. Symptoms noticed before complete collapse is dry and hot skin, shallow and rapid breathing, apparent exhaustion, and fatigue even after rest. As the core body temperature rises, the victim may become listless and confused, and may make little or no attempt to keep cool off. Pain in the extremities can be the first warning of dangerous exposure to heat. If the body core temperature increases to above 106° F, a significant and dangerous reduction in the blood pressure, and increases in pulse rate and respiration can occur. In extreme cases, death may occur.

- Dehydration - can occur, in absence of heatstroke, when the body does not receive sufficient fluid to replenish the liquid exhausted by sweating. The symptoms are dry lips and tongue, apathy and lack of energy, muscle cramping and bright colored or dark urine.

The potential for both heat and cold related disorders or conditions can occur in many common situations. Cold early morning temperatures can give way to warm daily temperatures, resulting in heavy perspiration within protective clothing. As temperatures cool again in the evening, the potential for cold related disorders or conditions can occur. Managers should be aware of the potential for this occurrence and should monitor workers accordingly.

Other physical hazards include noise, and wet conditions that could present slipping or falling hazards. There is also machine related hazards (i.e., clothing getting caught in the pumps.)

4.5 Task Hazard Analysis

The site activities will be intrusive, and the potential hazards associated with the sampling activities include inhalation hazards, dermal exposure, cold and heat stress, and noise physical hazards associated with the operation of the pilot system. Table 4-3 provides a task hazard analysis for the field activities to be conducted at Redstone Arsenal.

Table C-4. Task Hazard Analysis

FIELD ACTIVITY	POTENTIAL HAZARD	HAZARD CONTROL MEASURES	PROTECTIVE EQUIPMENT
Non-Intrusive Work (site walkovers, field survey, site preparation for intrusive activities)	Slips, trips, falls	<ul style="list-style-type: none"> • Watch where you are stepping • Avoid areas of debris, thick vegetation • Use caution when walking near steep slopes 	Work in Level D (standard work clothes) personal protective equipment (PPE) except in site locations where Level C is required. Any changes in the level of PPE required based on site conditions.
	High or low ambient temperatures	<ul style="list-style-type: none"> •Wear proper work clothes •Monitor for heat (if wearing impermeable protective ensemble) or cold stress 	
System Setup and Transport	Slips, trips, falls	<ul style="list-style-type: none"> • Watch where you are stepping • Avoid areas of debris, thick vegetation • Use caution when walking near steep slopes 	Work in Level D PPE (standard work clothes). Any changes in the level of PPE required based on site conditions, such as the potential for contact with visibly contaminated surfaces or waters, will be the responsibility of the designated SSHO.
	Machinery and rotating equipment	<ul style="list-style-type: none"> • Avoid standing near operating/rotating drilling equipment • Avoid turning back on operating drill rig • Stand far enough away from operating machinery to prevent accidental contact that could result from mechanical or human error. 	
	Overhead and underground utilities	<ul style="list-style-type: none"> • Keep operating equipment clear of overhead utility lines or other overhead hazards. For electrical wires less than or equal to 50 kV keep a minimum clearance of 10 feet. For electrical line greater than 50 kV, maintain a minimum clearance of 10 feet plus 0.4 inches per kV above 50 kV. • Contact dig-safe and local/site utility representatives to locate/mark underground utilities prior to excavating 	
	Dermal contact and inhalation of hazardous substances	<ul style="list-style-type: none"> • Work in well ventilated area and monitor breathing zone of work area for hazardous chemical vapors, mix chemicals with proper ventilation. • Utilize Modified Level D PPE if dermal contact hazard (See Section 5.2 for description of PPE) • Utilize Level C PPE including full-face APR, chemical resistant gloves, boots, and coveralls if inhalation hazard cannot be controlled (See Section 5.2 for description of PPE) 	

FIELD ACTIVITY	POTENTIAL HAZARD	HAZARD CONTROL MEASURES	PROTECTIVE EQUIPMENT
	Handling heavy objects	<ul style="list-style-type: none"> Observe proper lifting techniques Obey sensible lifting limits Use mechanical lifting equipment to move large, awkward loads 	
	Sharp objects	<ul style="list-style-type: none"> Wear cut resistant work gloves when possibility of lacerations or other injury from sharp objects exists Maintain all hand and power tools in a safe condition 	
	High noise levels	<ul style="list-style-type: none"> Use hearing protection when exposed to high noise levels (i.e., rule of thumb – when necessary to raise one’s voice to communicate with others three to five feet away). 	
	Low ambient temperature	<ul style="list-style-type: none"> Wear proper work clothes Monitor for cold stress 	
System Sampling	Slips, trips, falls	<ul style="list-style-type: none"> Watch where you are stepping Avoid areas of congestion, piping, hoses Use caution when walking near slippery, wet conditions 	Work in Level D PPE (standard work clothes). Any changes in the level of PPE required based on site conditions, such as the potential for contact with visibly contaminated surfaces or waters, will be the responsibility of the designated SSHO.
	Sharp objects	<ul style="list-style-type: none"> Wear cut resistant work gloves when possibility of lacerations or other injury from sharp objects exists Maintain all hand and power tools in a safe condition 	
	High ambient temperature	<ul style="list-style-type: none"> Wear proper heat stress 	
	Dermal contact and inhalation of hazardous substances	<ul style="list-style-type: none"> Work in well ventilated area and monitor breathing zone of work area for hazardous chemical vapors, mix chemicals with proper ventilation. Utilize Modified Level D PPE if dermal contact hazard (See Section 5.2 for description of PPE) Utilize Level C PPE including full-face APR, chemical resistant gloves, boots, and coveralls if inhalation hazard cannot be controlled (See Section 5.2 for description of PPE) 	
Online Monitor Maintenance	Slips, trips, falls	<ul style="list-style-type: none"> Watch where you are stepping Avoid areas of congestion, piping, hoses Use caution when walking near slippery, wet conditions 	Work in Level D PPE (standard work clothes). Any changes in the level of PPE required based on site conditions, such as the potential for contact with visibly contaminated surfaces or waters, will be the responsibility of the designated SSHO.
	Dermal contact with hazardous substances	<ul style="list-style-type: none"> Work in well ventilated area Utilize Modified Level D PPE if dermal contact hazard (See Section 5.2 for description of PPE) Utilize Level C PPE including APR, chemical resistant gloves, boots, and coveralls if inhalation hazard cannot be controlled (See Section 5.2 for description of PPE) 	

FIELD ACTIVITY	POTENTIAL HAZARD	HAZARD CONTROL MEASURES	PROTECTIVE EQUIPMENT
	Sharp objects	<ul style="list-style-type: none"> • Wear cut resistant work gloves when possibility of lacerations or other injury from sharp objects exists • Maintain all hand and power tools in a safe condition 	
	High ambient temperature	<ul style="list-style-type: none"> • Wear proper heat stress 	

5. Hazard Monitoring and Control

5.1 Training

All personnel who perform field activities during the demonstration at the Redstone Arsenal must be familiar with the operation and maintenance procedures of the field demonstration system. All personnel, including ARA subcontractors, performing site activities must be trained on the operation of the system. See Section 8 (RECORDKEEPING) for additional details.

In addition, a safety meeting conducted by the site safety officer shall be held prior to field activities to reiterate the health and safety requirements or to inform site personnel of upcoming operations and safety requirements.

5.2 Personal Protective Equipment

Personal protection requirements for personnel will be established at Level D based on an initial assessment of hazards at the site. Level D protection is the minimum basic work uniform worn for any site operation and will be used at all times by on-site personnel engaged in sampling when working at the site. The Level D protection scheme consists of the following protective equipment:

- Chemical resistant glove; shall be worn if environmental samples or contaminated equipment are handled (Granet; Nitrile 492)
- Safety Glasses; shall be worn while operating machinery or sampling
- Safety or chemical-resistant boots (personal work boots or Rainfair; ANSI #Z41.1-1972-75) shall be worn at all times
- Chemical-resistant coveralls (E.I. Dupont de Nemours & Company Tyvek suits); shall be worn if environmental samples or contaminated equipment are handled
- Hardhat (Mine Safety Appliance Company, V-Guard); shall be worn as required.
- Ear Plugs/Muffs; will be worn as necessary

An upgrade to Level C protection is warranted under the following three conditions:

- When air purifying respirators can sufficiently protect personnel from the chemicals
- When IDLH concentrations of suspected chemicals are not expected
- When exposure of unprotected area of the body (i.e., neck and back of head) to the chemical is not likely to cause harm.

Level C protection consists of the following personal protective equipment:

- Full-face air-purifying respirator (APR) with organic vapors/HEPA cartridges
- Tyvek coveralls
- Vinyl inner gloves
- Chemical-resistant steel-toed boots and disposable boot covers, if necessary

- Hard hat
- Hearing protection (ear plugs/ear muffs).

The sampling team will use Level C protection if a respiratory hazard due to dust and/or chemical/hydrocarbon vapor is determined to be present. If organic vapors exceed 50 ppm in the breathing zone, all personnel shall leave the site and contact the ARA Program Safety Officer for direction. At that time, the ARA Project Manager and Program Safety Officer will evaluate the situation. It is expected that Level D or Level C protection will be adequate for all field activities conducted for this project. **The use of Level B protection is not authorized by this plan.** If the SSC determines that Level C is insufficient per the requirements in this section, the field team will withdraw from the site and a revised HASP will be prepared.

A full complement of spare protective equipment will be kept at the site so that damaged or malfunctioning equipment can be replaced immediately.

5.3 Emergency Equipment

In spite of safety and health training, the use of appropriate protective equipment, and exercise of due caution by members of the site teams, the possibility exists for injury and illness in the field. In order to provide emergency assistance to sick or injured workers, the following supplies and equipment will be available on site:

- Potable water or Gatorade with ice (one to two gallons per person);
- First aid kit containing supplies for initial treatment of minor cuts and abrasions, severe lacerations, shock, heat stress, eye injuries, skin irritation, thermal and chemical burns, snake and insect bites, and immobilization of fractures;
- Cellular phones; and a
- Fire Extinguisher.

5.4 Monitoring and Sampling Plan

The sampling events associated with the demonstration are planned for an open environment with adequate ventilation. Therefore, no planned air sampling and air monitoring events are planned. If deemed necessary, occupational noise levels will be measured using a sound level meter during drilling activities and ambient air monitoring may be performed with the following equipment:

- PID - HNu system portable PID equipped with an 11.7 electron volt UV lamp. This instrument shall be maintained and calibrated every day according to the Mini RAE operations manual;
- Combustible gas indicator (CGI);
- Carbon monoxide detector;
- Personal air sampling pumps with filter cassettes; and a
- Sound level meter.

If air monitoring is deemed necessary, air monitoring logs will be maintained. These logs will contain the names of all personnel performing work at the site, a description of the work being performed at the site, and any new procedures established for performing work. In addition, these logs will list the types of air monitoring equipment being used; how and when this equipment was calibrated; air monitoring results; the level of personal protective equipment being used; and complete descriptions of all injuries, accidents, physical complaints, and unusual occurrences. Table 5-1 lists the site actions that are required for detected concentrations for each detection instrument.

Table C-5. Action Limits for Site Contaminants

Monitoring Instrument	Detected Concentration	Site Action
PID/FID	> 5 ppm for 1 minute	Upgrade PPE to Level C
PID/FID	> 50 ppm for 1 minute	Leave site and contact HSO
CGI	10 percent LEL	Leave site and contact HSO
Personal Air Samples	0.05 f/cc	Upgrade PPE to Level C

5.6 Site Control Measures

Personnel may be required to work alone during the performance of sampling activities. As a safety measure, a cellular phone will be available on site to summon emergency assistance. If personnel are on site alone, they will notify the Field Manager or Site Safety Coordinator. Other site control measures include the following:

- The initial indoctrination of site personnel and site-specific safety training will be accomplished during a training session conducted by the SHSO. In addition, site personnel will receive a site orientation and review of the HASP.
- Emergency phone numbers (Provided in Attachment 3) for the fire department, ambulance service, nearest medical clinic/hospital, along with the quickest traveling route to the hospital shall be available.
- A tailgate safety meeting will be conducted at the beginning of each shift, whenever new personnel arrive at the job site, as site conditions change, or when deemed necessary. They will be conducted by the Field Manager or Site Safety Coordinator to discuss pertinent site safety topics.
- The SSC will ensure that appropriate PPE is available and used and described in Section 4 of this HASP.
- ARA will emphasize compliance with state, local, and motor vehicle laws and regulations. Special considerations such as current or anticipated hazardous road conditions will be addressed.

5.7 Decontamination Plan

It is not expected that personnel or equipment performing investigative activities on this site will become contaminated to concentrations considered hazardous. However, to ensure that potential contaminants are not carried offsite, the following decontamination procedures shall be implemented.

Level D Decontamination: Site sampling tasks at the site will be conducted in Level D protection unless criteria for upgrading to Level C protection are exceeded. Personnel decontamination is required prior to crossing the designated hotline at the entry/exit point of the exclusion zone, and will consist of the following:

- When exiting the exclusion zone prior to crossing the hotline, personnel shall remove overboots, disposable coveralls and outer work gloves. This will entail removal of protective clothing in an “inside out” manner. Removal of contaminants from clothing or equipment by blowing, shaking, or any other means that may disperse material into the air will be prohibited. The coveralls and gloves are disposed of in a plastic bag. Rubber overboots may be left at the decon station for re-use in the area during the next sampling activity.
- Monitoring equipment including personal sampling pumps and ring badges/dosimeters will be removed and rinsed or wiped down with soap and water.
- Personnel will not be permitted to exit the exclusion zone until they have washed their hands and face with soap and water.
- At the conclusion of work in a site exclusion zone, all protective equipment will be placed in plastic bags for proper disposal or transfer off site.

Level C Decontamination: This decontamination procedure will follow the same discussed above for Level D decontamination, with the air-purifying respirator (APR) being the last item removed prior to exit from the exclusion zone. The respirator will be cleaned with a solution of soap and water, and the cartridges will be disposed of if the existing cartridges are loaded with particulate or wetted during decontamination.

5.8 Sanitation

Sanitary toilet facilities and potable water will be provided for all field personnel at Redstone Arsenal by the existing facilities, adjacent to the test site (Buildings 7741).

5.9 Confined Space Entry Plan

There will be no confined space entry requirements during this project. ARA personnel are not authorized to conduct any confined space entries.

5.10 Enforcement of the Site Specific Health and Safety Plan

5.10.1 Inspections

The SSC is responsible for ensuring that the HASP is being effectively implemented. The SSC will document the following, at a minimum:

- Verification that all ARA field personnel are in compliance with OSHA regulations for hazardous waste site work;
- Verification that PPE is being properly used; and
- Documentation of any deficiencies and actions taken to correct the deficiencies.

5.10.2 Audits

The ARA Health and Safety Officer or a representative will be onsite initially to evaluate compliance with the HASP. No audits by ARA are planned. If an independent inspection is conducted by a regulatory agency while ARA is on site, ARA personnel should follow the instructions in ARA EC&HS Procedure 24 - Regulatory Agency Inspections and Incident Reporting.

5.10.3 Project Debriefing

The Program Manager will conduct a debriefing with ARA site personnel to identify any problems that may have arisen during the inspection. This briefing will include any deviations from the HASP, reasons for the deviations, and potential risk to site personnel.

The debriefing will be prepared by the SSC by completing the Hazardous Waste Site Task/Project Debriefing Questionnaire (Attachment 4) and be reviewed by the Program Manager within 30 days of the date of the last activity at the site.

5.10.4 Health and Safety Plan Amendments

It is not anticipated that the HASP will require changes. If field conditions are different than anticipated or other conditions change, this plan may be amended by completing a Field Change Request Form, included in Attachment 5.

6. Emergency Response

6.1 Site Emergency Response

The types of emergencies that could occur include the following:

- Heat stress related illnesses;
- Injuries from Slips, trips, or falls;
- Motor vehicle-related accidents or injuries;
- Chemical contact/splashing during decontamination of equipment; and
- Machinery and mechanical equipment related injuries

It is the objective of this HASP to minimize chemical and physical hazards and operational incidents. The following information is provided to ensure that personnel respond to an emergency situation in a calm, reasonable manner. Prior to commencement of field operations, an emergency medical assistance network will be established. Telephone numbers for the fire department, ambulance, and hospital/medical clinic with an emergency room and locations/routes for the emergency room facility will be available for immediate reference by field staff (Attachment 3). Personnel will be equipped with a cellular phone to assist in summoning assistance, and a vehicle will be available on site at all times to transport injured personnel to the emergency facility if required. The following procedures will be followed:

- The SSC is the lead in all emergency situations;
- A fully stocked first-aid kit will be available on site for immediate assistance;
- An adequate supply of fresh potable water and portable emergency eye wash stations will be available at each work site;
- Site personnel will be trained in emergency procedures during site orientation;
- Evacuation routes from each sampling site will be established by the SSC, and communicated to all field personnel during the Tailgate Safety Meeting before each work shift; and
- The SSC will be responsible for ensuring that all ARA personnel understand site-specific emergency signals and procedures.

6.2 Personnel Injury

General first-aid procedures are included in this section. General first aid procedures include:

- Skin Contact—Use copious amounts of soap and water. Rinse the affected area for at least 15 minutes; then provide appropriate medical attention. Eyes should be rinsed for a minimum of 15 minutes upon chemical contamination.
- Inhalation—Move to fresh air and, if necessary, decontaminate, and transport to the hospital.

- Ingestion—Transport to the hospital.
- Physical Trauma, Puncture Wound, or Laceration—Stop the bleeding, stabilize, treat for shock, and transport to emergency medical facility.

In the event of an injury, the victim should be stabilized and provided onsite first aid in the "clean zone." If an injury involves a potential trauma to the spinal cord, the victim shall remain where injured, if safely possible, and be moved by trained emergency medical technicians only. Minor injuries such as small lacerations, cuts, and strains shall be initially treated onsite by a first aid qualified member of the field team. Ambulance and hospital support shall be provided for all major injuries, such as head wounds, broken bones, and deep lacerations.

If decontamination is required and does not interfere with essential treatment, the following should be performed:

- Escort victim to the decontamination station;
- Wash, rinse, or cut off protective clothing and equipment;
- Wash exposed body areas with a potable water flush (10 minutes);
- Cover with blanket or (if injury is not serious) dress victim in clean clothing; and
- Transport victim to hospital if necessary or request ambulance support, if needed.

If decontamination is required, but cannot be performed, the following should be completed:

- Wrap the victim in blankets, plastic, or rubber to reduce contamination of other personnel
- Alert emergency and offsite medical personnel to potential contamination; instruct them in specific decontamination procedures, if necessary
- Send along site personnel familiar with the incident.

Should an accident occur, the SSC will complete an accident report and investigate the cause. Accidents must be reported by telephone to Program Manager as soon as possible, but not later than 2 hours after occurrence and reported in writing within 5 days of occurrence. All other incidents must be reported by telephone, within 8 hours of occurrence, or sooner if conditions permit. Any recommended hazard control must be discussed with the ARA Health and Safety Manager and meet his approval prior to implementation. Any chemical exposure or occupational injuries and illnesses also shall be reported and recorded, if recordable per 29 CFR 1904, on OSHA Form No. 200. Records of all site accidents and first aid treatments will be maintained by the SSC.

First aid and CPR is considered to be a collateral duty, not a primary assignment. In the event an injury occurs and an individual rendering first aid is exposed to blood or other potentially infectious materials, the person(s) exposed must be provided with follow-up medical surveillance in accordance with 29 CFR 1910.1030(f)(1).

6.3 Telephone/Radio contact Reference List

In many cases, communications will not be readily accessible in the field. In an emergency situation, an individual will be immediately dispatched to contact appropriate emergency response individuals by telephone. If a life threatening injury precludes decontamination of a contaminated individual, the Emergency Response personnel or Fire Department will be contacted immediately by telephone. First aid will be performed if it does not endanger the safety of the individual administering first aid.

Prior to commencement of field operations, an emergency medical assistance network will be established. A vehicle will be available onsite during all activities to transport injured personnel to the identified emergency medical facilities. Additional safety provisions will be made as follows:

- A cellular phone will be available to assist in summoning assistance;
- Telephone numbers of the emergency room facilities and their locations will be posted at the site (including the fastest routes to the emergency facilities);
- The SSC or a designated alternate will be the lead in all emergency situations;
- A first-aid kit will be available at the site;
- An adequate supply of fresh water and portable emergency eyewash will be available at the work site; and
- Evacuation routes from each specific sampling area will be established by the SSC, and communicated to all personnel during the tailgate safety meeting conducted before each work shift.

Attachment 3 provides a list of the emergency/reference numbers to be used during the sampling at the site.

6.4 Changes In Anticipated Conditions

Should unanticipated conditions occur (e.g., encounters with chemical or biological agents, hazardous waste materials, toxic substances), ARA personnel will immediately evacuate the area. A reevaluation of site conditions will be conducted by the SSC. Required changes should be noted on the Field Change Form (Attachment 5) and sent to the EC&HS Officer. Appropriate modifications will be incorporated into the plan before resuming work.

6.5 Accident Reporting

Accidents/Incidents must be reported as soon as possible, but not later than 2 hours after the occurrence and reported in writing within 1 day of occurrence on the form in Attachment 2. All accidents and/or injuries shall be immediately reported to the Site Safety Officer. An accident report and, if necessary, an exposure report will be initiated by the Site Safety Officer and provided to the Program Safety Officer for processing. An accident reporting form is provided in Attachment 2.

Exposure to a toxic agent may often have delayed or latent effects which can only be detected by specific diagnostic tests. Documenting an exposure may aid in identifying the cause of symptoms or changes in health status indicators (e.g., diagnostic blood tests or pulmonary functions) at a later time. Similarly, physical injuries (e.g., an eye injury caused by dust particles or solvents) may also result in delayed damage to the eye.

The field report will be reviewed and signed by the SSC and forwarded to the ARA EC&HS Officer for review. In addition, the person in charge during the incident will prepare a written report on the actions taken during the incident and follow-up. The reports will be submitted using the Hazardous Waste Site Task/Project Debriefing Questionnaire (Attachment 4) to the ARA EC&HS Officer. The ARA EC&HS Officer will determine the need for further follow-up actions.

6.6 Fire Emergencies

In the event of a fire, attempts will be made to extinguish it with a Class A, B, or C fire extinguisher, if safe to do so. If the fire appears to be growing "out of control," the following steps will be performed:

- The field team should depart the site;
- Verify all present;
- Notify the Fire Department;
- Remove vehicles if safely possible;
- Remove flammable field solvents and fuels if safely possible;
- Await fire-fighting forces; and
- Contact the Project Manager and the ARA Program Safety Officer once the Fire Department is in control of the situation.

7. Hazardous Material Release

In the event a hazardous material release occurs during site activities, attempts may be made to control, divert, absorb, neutralize, or secure the source if direct contact or inhalation hazards are not present. If direct contact or inhalation hazards are present, remedial measures should not be attempted. All hazardous material release incidents shall be reported to the ARA Program Safety Officer as soon as possible.

The following information will be helpful during a notification:

- Chemical/oil name or U.S. Department of Transportation (DOT) I.D. number;
- Cause of release;
- Quantity/concentration of the release;
- Potential for fire;
- Potential for site release evaluation;
- Injuries caused by release; and
- Actions taken.

8. Recordkeeping

Record keeping requirements for health and safety are discussed in Chapter 20 of the ARA Environmental Compliance and Health and Safety Manual. A list of records that should be maintained for this demonstration is provided in Table 8-1.

Table C-6. Record Keeping

Record Kept	Frequency	Documentation
Accident/Incident Reports	As needed	Logbook and separate reports
Inspection of Safety Glasses	Daily	Logbook, if defective
Noise	When hearing protection required	Logbook
Personnel Medical Monitoring	Annual records	Personnel file, copy with worker On site
Temperature/ Weather Conditions	Daily	Logbook
Training of Employees	Annual training records	Personnel file, copy with worker on site

A Supervisor's Accident Investigation Report form is provided as Attachment 3.

9. REFERENCES

The following references were used in writing this plan and may provide more information on site health and safety:

American Conference of Governmental Industrial Hygienists, *2000 TLVs and BEIs, Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*.

29 *CFR* 1910.120, "Hazardous Waste Operations and Emergency Response".

29 *CFR* 1910.1200, "Hazard Communication".

29 *CFR* 1910.1000, "Air Contaminants - Limits for Air Contaminants".

NIOSH Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, June 1997.

ARA Environmental Compliance and Health and Safety Manual. Available upon request.

ARA Attachment 1 - Personal Acknowledgment Form

PERSONAL ACKNOWLEDGMENT

As a component of the Health and Safety Plan (HASP), designed to provide safety for the field activities to be conducted during the ESTCP Field Demonstration at Restone Arsenal, Huntsville Alabama, you are required to read, understand, and agree to abide by the provisions in the HASP.

By my signature, I certify that I have read, understand, and will abide by the ARA Health and Safety Plan for the ESTCP Ion Exchange Demonstration.

Signature

Date

ARA Attachment 2: Supervisor's Accident Investigation Report

Instructions for Parts III and IV are given on the following page. If more space is needed in completing the report, use additional pages. Complete and return this report to the Local EC&HS Official no later than the next working day after the accident.

Part I:

General Information

Name of Injured: _____ Division: _____
Location: _____ Employee Number: _____
Date of Accident: _____ Hour: _____ AM/PM Exact Location: _____
Name of Witness: _____ Division: _____

Part II:

Description of Accident (*Summarize the accident, providing specific detail.*)

Part III: Causes of Accident (*Determine the cause by analyzing all involved factors, including those listed in the instructions.*)

A. Describe Any **Unsafe** Acts: _____

B. Describe Any **Unsafe** Conditions: _____

ARA Attachment 2: Supervisor's Accident Investigation Report (Continued)

Part IV: Corrective Action Taken (*Summarize actions taken and recommendations made to prevent a similar accident or recurrence of the same accident. Before completing this section, study the steps identified in the instructions.*)

If no actions have been taken, give the reason(s) _____

Signatures: _____
Supervisor Local EC&HS Official

Date Report Prepared: _____

ARA Attachment: Supervisor's Accident Investigation Report Instructions (Continued)

Part III: Accident Causes. *Use the following lists in determining the cause(s) of the accident.*

Selected Unsafe Acts-Personal Factors

Making safety devices inoperable
Failure to use guards provided
Using defective equipment
Servicing equipment in motion
Failure to use proper tools or equipment
Operating machinery or equipment at unsafe speed
Failure to use personal protective equipment
Operating without authority
Lack of skill or knowledge
Unsafe loading or placing

Improper lifting, lowering, or carrying
Taking unsafe position
Unnecessary haste
Influence of alcohol or drugs
Physical limitation or mental attitude
Unaware of hazards
Unsafe act of other

Selected Unsafe Conditions

inadequate guards or protection
Defective tools or equipment
unsafe condition of machine
Congested work area
Poor housekeeping
Unsafe floors, ramps, stairways, platforms
improper material storage
Inadequate warning system
Fire or explosion hazards
hazardous atmosphere: gases, dust, fumes, and vapors
hazardous substances
Inadequate ventilation
Radiation exposures
Excessive noise
Inadequate illumination

ARA Attachment 2: Supervisor's Accident Investigation Report Instructions (Continued)

Part IV: Corrective Action Taken. *Take the following steps to prevent a similar accident or recurrence of the same accident.*

1. Discuss the accident with the employee involved and with any witnesses. Be sure to question the what-where-when-who-how-why aspects of the accident.
2. Inspect the equipment or materials involved for conditions that can be made safer.
3. Study the job setup and manner of doing the work and decide if improvements can be made.
4. Determine if the employee involved is suited for the job he or she is doing, if the employee received adequate training, and if there are any other problems.
5. Develop practical recommendations to correct the problem. Be sure your recommendations will not create other situations that could result in injury to employees.

Documentation and Recordkeeping

Attachment 3 - Emergency Contacts

Emergency Telephone Number Reference List	
Responder	Number
Police Department	911
Fire Department	911
Huntsville Hospital, Main 101 Sivley Road SW Huntsville, AL 35801	256-517-8020
Andrea Davis – ARA Project Manager	850 914-3188 850-258-2092 (cell)
Jeff Rine, Steve Baxley, Andrea Davis, Robert Girvin, Nick Alford, Edward Coppola- Site Safety Coordinator	850 914-3188 850 896-5389 (cell)
Wes Smith – Restone Arsenal Manager	256- 876-9479
Andrea Leeson, PhD – ESTCP	703- 696-2118

**ARA Attachment 4: HAZARDOUS WASTE SITE TASK/PROJECT
DEBRIEFING QUESTIONNAIRE**

The purpose of this questionnaire is to serve as a checklist for documenting a formal review of environmental compliance & health and safety (EC&HS) status upon completion of a field effort at a hazardous waste site. This form is to be prepared by the SSC (or individual designated by the Project Manager) and reviewed by the Project Manager or other cognizant manager within 30 days of the date of last activity at a site.

Site Name: _____

Applicable SSHSP (title, date): _____

Duration of site work covered by this debriefing:

Start Date: _____

Completion Date: _____

4. List ARA Employees who worked at this site:

Name	Employee No.	Name	Employee No.
1.		6.	
2.		7.	
3.		8.	
4.		9.	
5.		10.	

Attach additional list on reverse of this page.

5. List subcontractors to ARA who worked at this site:

Subcontractor Name	Address	Task

6. Were there any accidents or injuries involving ARA or subcontractor personnel that required medical treatment? Yes/No _

If yes, give names of individual(s), date(s) or injury, and attach a copy of the supervisor's accident investigation report:

Name	Date	Employer
1.		
2.		
3.		

7. Did the subcontractors comply with applicable health and safety requirements?

Yes/No

If no, give details: _____

8. Were there any unplanned releases of contaminated material to the environment (spills to navigable water, non compliant discharges to a POTW)? Yes/No

If yes, what notifications were made (e.g. National Response Center, client, EPA, or State Agency)? Attach relevant correspondence.

9. Were employee exposures to chemical hazards monitored? Yes/No

If yes, complete the following:

A. Monitoring using OVA or Hnu Instrument:

Action level stated in the SSHSP: .

Was action level ever exceeded: Yes/No

If yes, indicate date(s) and action taken.

Date	Action

B. Monitoring using chemical-specific devices (such as Draeger tubes, H₂S monitor, samples collected for laboratory analysis):

Substance Measured	PEL	BZ or Area	Lowest Measured Exposure	Highest Measured Exposure	Respiratory Protection Used (Yes/No)
1.					
2.					
3.					
4.					
5.					

Comments: _____

10.A. Were employee exposures to noise measured at this site? Yes / No

If yes, attach applicable reports.

B. List significant sources of noise (indicate type of drill rig, compressors, pumps, and other noise generating equipment)

1. _____
2. _____
3. _____
4. _____

C. Was hearing protection required? Yes / No

If hearing protection was required, was it provided? Yes / No

D. Was the use of hearing protection in high noise areas enforced? Yes / No

11. Were radiation hazards monitored at the site? Yes / No

If yes, complete the following:

Types of radiation: ___ alpha ___ beta ___ gamma

Isotopes: __

Airborne radioactive contamination _____

Non-Airborne radioactivity (fixed contamination, sealed sources, etc.) _____

Cumulative radiation doses for site workers by job category (i.e., rig geologist, supervisor, field technician, visitors, subcontractors, other)

Job Category	Cumulative Dose (millirem)	Number of Employees Per Category

12. Were any unusual conditions encountered at this site? Yes / No

If yes, please explain: _____

13. Describe any lessons learned at this site, regarding hazard identification and control that should be communicated to other ARA personnel working at hazardous waste _____

Prepared By: _____ **Date:** _____

Reviewed By: _____ **Date:** _____

ARA Attachment 5: Field Change Request

<div style="display: inline-block; width: 20%;">ARA</div> <div style="display: inline-block; width: 80%;">FIELD CHANGE REQUEST</div>
<div style="display: flex; justify-content: space-between;"><div>Field Charge No: _____</div><div>Page of ____ of ____</div></div> <div>Project Number: _____</div> <div>Project Name: _____</div>
Change Request Applicable Reference: _____ Description of Change: _____ _____ Reason for Change: _____ _____ Impact on Present and Completed Work: _____ _____ Requested by: _____ Date: _____ <div style="text-align: center;">(ARA Field Geologist/Engineer)</div> Acknowledged by: _____ Date: _____ <div style="text-align: center;">(Subcontractor Representative/Company Name)</div>
Field Operations Manager Recommendation Recommended Disposition: _____ _____ Recommended by: _____ Date: _____ <div style="text-align: center;">(ARA Field Operations Manager)</div>
Health and Safety Review Approved/Disapproved by: _____ Date: _____ <div style="text-align: center;">(ARA Qualified Individual)</div>
Project Manager Review Final Disposition: _____ _____ Approved/Disapproved by: _____ Date: _____ <div style="text-align: center;">(ARA Project Manager)</div>

Appendix D

Tests using Rohm and Haas Resin PWA2

January 13, 2006

**ESTCP PROJECT NUMBER CU-0312
ARA PROJECT NUMBER 16623**

PWA2 Regeneration Test

Rohm and Haas resin, PWA2, was one of the strong base anion resin candidates screened for this demonstration. Although PWA2 has high capacity and selectivity for perchlorate, there is no reported procedure for regenerating the resin. However, it was determined during resin screening that PWA2 is also very selective for nitrate. A batch study was conducted to determine if PWA2 resin loaded with perchlorate could be regenerated using a concentrated nitrate regenerant solution.

Batch Study

Variables in these batch studies included nitrate concentration (1 to 8 molar solutions), nitrate species (i.e. sodium nitrate and ammonium nitrate), and pH. To evaluate the ability for concentrated nitrate solutions to displace perchlorate, a known amount of PWA2 resin was loaded with perchlorate. The amount of perchlorate loaded on the resin in each batch was calculated using the concentration and volume of perchlorate solution added and the final concentration of perchlorate in solution with PWA2 after equilibrium. The resin used for each batch test had approximately 25 milligrams of perchlorate loaded. The nitrate regenerating solutions were prepared and added to the perchlorate loaded PWA2 resin batches for sampling and analyzing. Tetrachloroferrate (regenerant for Purolite resin A530E) and a control using distilled water were also tested.

Perchlorate was analyzed using EPA Method 314.0. A summary of perchlorate recovery results is provided in Figure D-1. No perchlorate was recovered in the distilled water control or the tetrachloroferrate batch. The pH of solutions did not seem to influence recovery. Based upon these results, a column test was designed to evaluate if perchlorate could be recovered from PWA2 resin using a 4M nitrate solution (no pH adjustment).

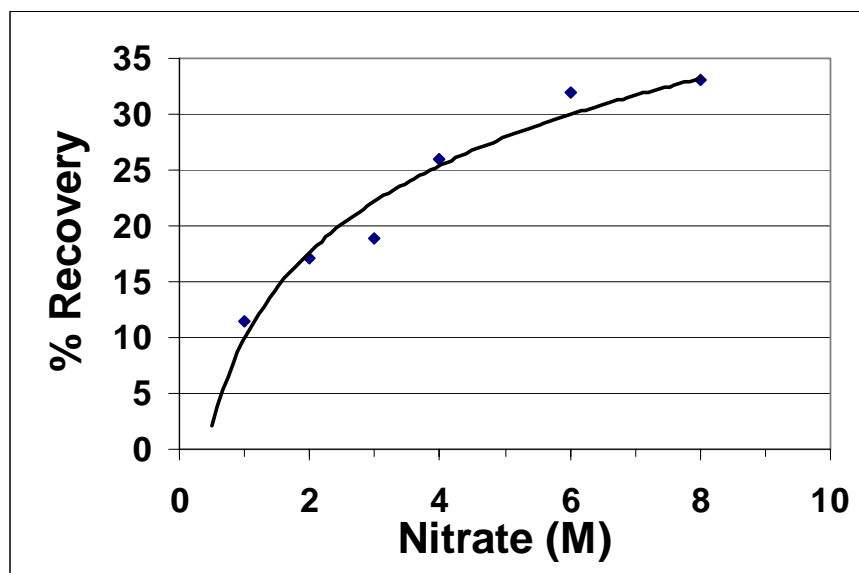


Figure D-1. Perchlorate Recovery in Batch Tests

A column was prepared holding 100 milliliters of PWA2 resin. The resin was loaded with 4.6 grams of perchlorate. This amount of perchlorate was calculated by knowing the concentration of perchlorate solution passed over the resin and the volume of this solution, and subtracting the perchlorate amount in the effluent. The perchlorate concentrations were determined using EPA Method 314.0. After the resin was loaded with perchlorate, a regenerant solution of 4M NO₃ was passed over the resin at a flow rate of 3.3 ml/min or approximately 2 bed volumes per hour. Samples were taken every bed volume (100 milliliters) and analyzed for perchlorate using EPA Method 314.0. Perchlorate recovery for each bed volume is provided in Figure D-2. The total recovery after 20 bed volumes of regenerant was passed over the resin was only 35%.

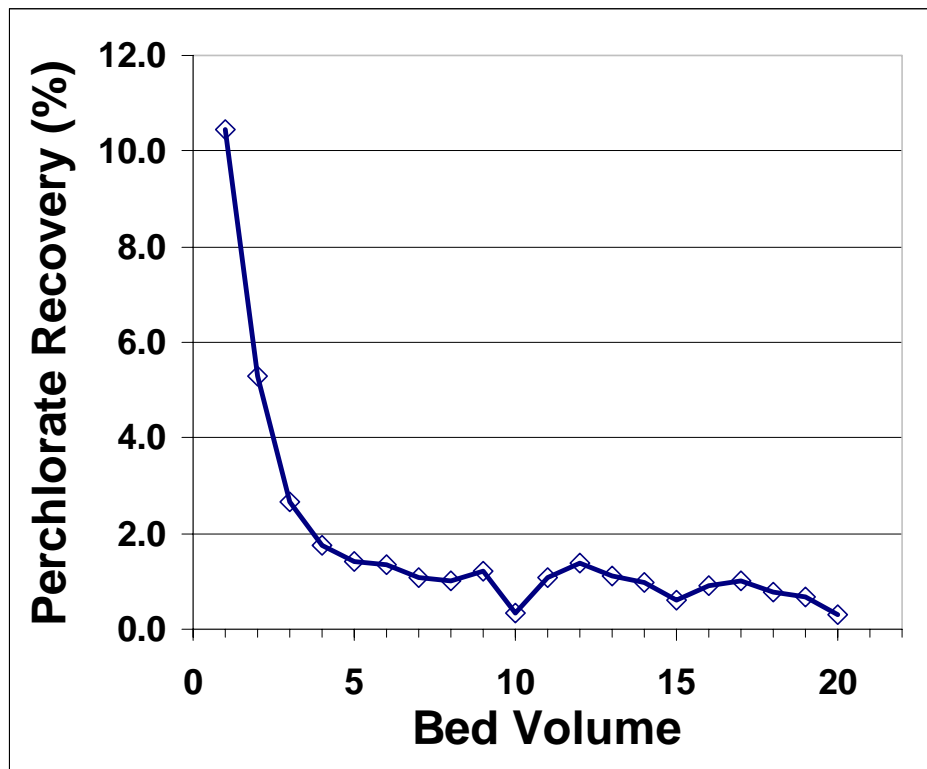


Figure D-2. Perchlorate Recovery during Column Flow Study

Although perchlorate was displaced using the 4M nitrate solution, efficiency of recovery was low as can be seen by the extensive tailing in Figure D-2. Results indicate that the volume of nitrate regenerating solution required for removing perchlorate from PWA2 would be prohibitive of a perchlorate remediation process using PWA2. No further testing was conducted.